1. Introduction

Biomass has the potential to become an abundantly available and renewable energy resource. Conversion of biomass into platform chemicals and fuels has been widely investigated recently\(^1\),\(^2\). Catalytic conversion of biomass is one promising approach\(^3\),\(^5\). Conversion of biomass and biomass-derived chemicals to gaseous fuels such as synthesis gas and hydrogen may allow production of liquid fuels and power generation\(^3\),\(^6\). However, competition of land for food and fuel production raises serious concerns, particularly as the current technology for first generation biofuel production depends on feedstock derived from the edible fraction of food plants (corn, rape seed, sugar beet and others). Therefore, conversion of abundantly available, renewable and non-edible lignocellulosic biomass, such as agricultural residues and food industry waste, into usable energy, fuels and chemicals is important. Unfortunately, conversion of non-edible lignocellulosic biomass to useful chemicals is not easy due to the complex hierarchical structure and chemical resistance of lignocellulosic biomass. Therefore, many types of catalytic technology for conversion of various non-edible biomass to useful fuels and chemicals have been investigated. Depending on the origin and production technology, biofuels are generally classified as first, second and third generation biofuels.

The present review describes the development and demonstration of biomass conversion technologies on both the laboratory and bench scale. Laboratory scale development of the novel catalyst and reactor for woody biomass conversion at relatively low temperature, and the development of novel catalytic conversion of glycerol to propanediols were carried out on the laboratory scale. In addition, the bench-scale BTL (biomass to liquid fuel) plant for biomass conversion and liquid fuel production was developed and demonstrated. Fischer-Tropsch (FT) synthesis diesel oil and dimethyl ether (DME) were produced from woody biomass by this bench-scale plant operation. Finally, continuous synthesis of DME over 600 h and recovery of approximately 1.1 kg of liquefied bio-DME were achieved. This bio-DME was used in the DME vehicle running test performed by the DME Vehicle Promotion Committee (DMEVPC).

2. Biomass Gasification Catalyst

Rh based catalysts are effective for the catalytic conversion of biomass and biomass-derived chemicals to synthesis gas on the laboratory scale\(^7\),\(^9\). However, the simple Rh/SiO\(_2\) catalyst exhibited high initial activity, but was easy to deactivate due to coking of the catalyst.
surface during the reaction. Therefore, our group has investigated the effect of CeO2 addition, which is well known as a promoter of the oxidation reaction due to its high oxygen storage capacity (OSC). Therefore, to enhance the catalytic activity and stability, Rh/CeO2/SiO2 catalyst (Rh: 1.2 wt%, CeO2: 30 wt%) was prepared by incipient wetness impregnation of CeO2/SiO2 support with an acetone solution of Rh precursor. To evaluate the catalytic activity, methane oxidation was carried out as a model reaction. Figure 1 shows methane conversion as a function of reaction temperature over Rh/CeO2/SiO2 and Rh/SiO2. Methane conversion decreased gradually with time on stream over Rh/SiO2. However, high and stable activity was obtained over Rh/CeO2/SiO2. In addition, Rh/CeO2/SiO2 also exhibited much higher activity and stability than Rh/SiO2 in partial oxidation of tar (POT) derived from the pyrolysis of wood biomass in a laboratory-scale continuous feeding dual-bed reactor.

The redox properties of these catalysts were investigated using the profiles of temperature programmed oxidation (TPO) and reduction (TPR). Figure 2 shows the TPO profiles of Rh/CeO2/SiO2 and Rh/SiO2. The TPO profile of Rh/CeO2/SiO2 differed greatly from that of Rh/SiO2. O2 consumption of Rh/CeO2/SiO2 was observed over a much lower temperature range than that of Rh/SiO2. O2 consumption of Rh/SiO2 is assigned to the oxidation of Rh species; the profile indicates that oxidation of the Rh metal particles on SiO2 proceeds more slowly at temperatures lower than 623 K. In contrast, oxidation of Rh/CeO2/SiO2 was almost complete below 700 K. This observation suggests that almost all Rh metal particles on Rh/CeO2/SiO2 interacted with CeO2. In addition, Rh-based oxidation was saturated at about 120 % over Rh/CeO2/SiO2, which indicates that Ce species oxidation corresponds to 20 % Rh-based oxidation.

The behaviors of the Rh-Rh, Rh-O-Ce, and Rh-O-Rh bonds during TPO experiments were investigated. Figure 3(a) shows that the CN of the Rh-Rh bond decreased, and that of the Rh-O bond increased remarkably with the TPO temperature. In particular, the contribution of the Rh-O-Ce bond was observed clearly at temperatures higher than 493 K, and was more remarkable than that of the Rh-O-Rh bond. This behavior of Rh/CeO2/SiO2 differs greatly from that of Rh/SiO2. The quick X-ray absorption fine structure (QXAFS) results suggest that Rh metal particles on CeO2/SiO2 are oxidized to Rh oxide species interacting with CeO2.

The TPR profile of Rh/CeO2/SiO2 identified two H2 consumption peaks at temperatures were lower than the peak on Rh/SiO2. These results indicate that the Rh species on Rh/CeO2/SiO2 is reduced more easily than that on Rh/SiO2. Therefore, addition of CeO2 to Rh/SiO2 promoted both oxidation and reduction of Rh species simultaneously, which contributed to the high catalytic activity for biomass gasification.

3. Propanediol Production from Glycerol

Glycerol is a common molecule with potential as an important biorefinery feedstock. Glycerol is a byproduct in the production of biodiesel by transesterification of vegetable oils. For example, glycerol can be converted to 1,2-propanediol and 1,3-propanediol. Recently, 1,3-propanediol production from fermentation of corn sugar has been commercialized and the utilization of 1,3-propanediol is expanding. In addition, glycerol hydrogenolysis is also important as a
model reaction of the reduction of more complicated biomass-related molecules such as sugars. Therefore, catalytic glycerol hydrogenolysis to propanediols has been extensively investigated, especially to develop effective catalysts for production of 1,2-propanediol[14] and 1,3-propanediol[15].

Combination of ion-exchange resin Amberlyst and Ru/C enhanced conversion and selectivity in glycerol hydrogenolysis. However, the details of the reaction mechanism were not clear. Therefore, we investigated the reaction scheme of glycerol hydrogenolysis and degradation, and discuss the formation route of hydrogenolysis and degradation products based on the catalytic activity for the formation of products and expected intermediates. We have carried out activity tests on Ru/C + Amberlyst 15 (A15) and Ru/C under similar conditions to those of glycerol hydrogenolysis to elucidate the reaction routes of the products. Here, we used 2 wt% aqueous solutions of each compound. Conversions of methanol, ethanol, 1-propanol, and 2-propanol were almost zero both over Ru/C and Ru/C + A15. Therefore, these compounds and methane are regarded as the final products in the reaction of glycerol. Generally, glycerol conversion over Ru/C + A15 was much higher than over Ru/C. On the other hand, the additive effect of Amberlyst was not great for the reactions of 1,2-propanediol, 1,3-propanediol, and ethylene glycol, indicating that the reactions of these three compounds are catalyzed by Ru/C. Comparison of the conversion levels showed that the reactivity order is 1,3-propanediol > ethylene glycol > 1,2-propanediol. The high reactivity of 1,3-propanediol is related to the low selectivity of 1,3-propanediol formation in the glycerol reaction. Therefore, 1,2-propanediol is formed mainly by dehydration of glycerol to acetol catalyzed by Amberlyst and subsequent hydrogenation of acetol to 1,2-propanediol catalyzed by Ru/C. The possible reaction route is shown in Fig. 4.

Based on these results, we investigated optimization of the Ru/C and Amberlyst catalyst for glycerol hydrogenolysis. Active carbon supported Ru catalysts were prepared from various active carbon materials such as Vulcan-XC72, Shirasagi DO-2, Shirasagi M and Carboraffin. The Ru/Vulcan-XC72 (Ru/XC) catalyst exhibited much higher activity for glycerol conversion. Comparison of the catalytic activity and characterization results such as BET surface area and metal dispersion suggested that lower surface area is more suitable, and the metal dispersion seems to be unrelated. On the other hand, the X-ray diffraction (XRD) measurement showed that the graphite phase was much clearer on Ru/XC than that on other catalysts, which suggests that Ru metal particles on the graphite phase have high catalytic activity. In addition, the CO and CO2 TPD profiles of support carbons clearly showed that desorption of CO and CO2 on XC72 was much lower than on other supports. Such desorption of CO2 and CO is due to decomposition of the surface functional groups such as carboxyl and carbonyl groups[16-18]. This result also indicates that XC72 has many fewer surface functional groups than other carbon supports. Therefore, carbon surfaces with fewer oxygen-containing functional groups such as carbonyl and carboxyl are more suitable as a support for Ru metal particles. Therefore, Ru/XC catalysts were selected as the high-performance catalyst for subsequent experiments.

The ion-exchange resin Amberlyst 15 exhibited adequate solid acid properties at milder reaction conditions, but the reaction temperature is limited by the highest operation temperature of the ion-exchange resin. Amberlyst 70 (A70) is a heat resistant ion-exchange resin with higher operation temperature than
A15. We applied the combination of the Ru/XC catalyst and heat resistant A70 for glycerol hydrogenolysis. Figure 5 compares the glycerol conversion between the developed catalysts and conventional catalysts. Enhancement of 1,2-propanediol production was achieved by the combination of Ru/XC and A70.

4. Liquid Fuel Production from Bench-scale BTL Plant Operation

4.1. Production and Storage of Synthesis Gas

The Biomass Technology Research Center, National Institute of Advanced Industrial Science and Technology (AIST) has constructed a bench-scale BTL plant (Fig. 6). Figure 7 shows the flow diagram of the proposed BTL process in the present study for woody biomass gasification using a fixed-bed gasifier, gas cleaning using a scrubber, removal of carbon dioxide, gas compression at more than 1 MPa, and liquid fuel production mainly by FT synthesis19).

The gasification step must effectively produce syngas from woody biomass without steam. The present study used oxygen-enriched air gasification in a down-draft fixed-bed gasifier, taking into account the produced tar concentration, applicability to small- or medium-scale plants, operation control, and operation energy requirements. CO2, which is an inert gas in the liquid fuel production reaction, was removed before the second gas compression to decrease energy needed for gas compression and the volume of high pressure gas. Figure 8 shows the change in temperatures of the combustion zone and reduction zone, and product gas flow rate with time. The reduction zone temperatures were stable whereas the combustion zone temperatures fluctuated. Char produced exothermically in the combustion zone was deposited in the reduction zone and

A15 = Amberlyst 15, A70 = Amberlyst 70, XC = Vulcun-XC72, T = 393 K or *453 K.

Fig. 4 Reaction Scheme of Glycerol Hydrogenolysis and Degradation

Fig. 5 Results of Activity Tests of Ru/C + Amberlyst

Fig. 6 Bench-scale BTL Plant (fixed-bed downdraft gasifier)
solids from the pyrolysis zone (lower temperature) were supplied to the combustion zone, which caused the variation in combustion zone temperature. Overall, stable biomass gasification could be achieved through operation of this BTL plant design. However, the syngas concentration of the product gas was not adequate for FT synthesis due to dilution by nitrogen introduced with the gasifying air. Therefore, oxygen-enriched air gasification was adopted using high oxygen concentration air.

Figure 9 shows the effect of oxygen content on the product gas composition from oxygen-enriched air gasification. Higher oxygen content resulted in increased concentration of CO from 26.0 to 41.9 vol%, and increased concentration of H₂ from 21.0 to 36.5 vol%, in contrast to decreased concentration of N₂ from 37.0 to 2.6 vol%. In addition, higher oxygen content also resulted in higher temperature in the reduction zone in the gasifier caused by promotion of the oxidation reaction. High temperature in the reduction zone is favorable for promoting the reforming of hydrocarbons, such as tarry compounds (C₅H₈ + CO₂ → CO + H₂, C₆H₆ + H₂O → CO + H₂), with CO₂ and H₂O produced in the combustion zone, which would lead to increased syngas yield with higher oxygen content. These developments have succeeded in the production and storage of synthesis gas with high H₂ and CO concentrations.

4. 2. Fischer-Tropsch Synthesis Fuel Production

FT synthesis is an exothermic reaction, but deposition of wax, which is a product, on the surface of the catalyst would lead to deactivation. Therefore, a liquid-phase FT synthesis reaction was employed, which has advantages over the common gas-phase reaction in terms of temperature control, wax extraction, and extension of catalyst lifetime. We have investigated a series of SiO₂ supported Mn and Zr modified Co catalysts with different preparation methods and various Mn, Zr loading for the FT synthesis reaction. Our investigations have suggested that enhancement of the FT synthesis activity of co-impregnation Co + Mn + Zr/SiO₂ catalyst is related to the formation of highly dispersed Co metal particles that interact with Mn species[20]. The modified Co + Mn + Zr/SiO₂ catalyst exhibited excellent FT synthesis activity in a lab-scale reaction.

To confirm catalytic activity on a large scale, the FT synthesis reaction on the bench-scale was investigated using the developed Co + Mn + Zr/SiO₂ catalyst. Synthesis gas was produced and stored using a bench-scale BTL gasifier and purified through a scrubber and desulfization towers. The final compressed gas composition was 59.5 % H₂, 28.5 % CO, 4.4 % CH₄, 7.5 % N₂, and 0.1 % CO₂. A bench-scale FT synthesis also was conducted using a slurry bubble column reactor system equipped with a 12.5 L volume reactor as described previously[19]. The catalyst used in this system was Co + Mn + Zr/SiO₂ catalyst (100-200 mesh, 250 g), reduced in-situ under a H₂ flow at 673 K and atmospheric pressure for 6 h before reaction. After cooling the reactor, 1.0 L of n-hexadecane was added to the reactor as a solvent. The FT synthesis reaction was conducted at 4.0 MPa for 6 h, with a syngas feeding rate for W/F of 3.0 g h/mol. The temperature of the slurry phase was maintained at approximately 500-530 K. Outlet gases were collected in a gasbag and analyzed using two gas chromatographs at fixed in-
tervals.

Figure 10 shows the changes in reaction temperature, inlet gas flow rate, and outlet gas flow rate with time during the bench-scale FT synthesis. The pressure remained constant at 4.0 MPa. Steady-state operation was achieved for approximately 5.5 h. The average CO conversion rate and C5+ hydrocarbon selectivity were 62.3% and 87.5%, respectively. C5+ yield and STY were 54.5% and 717 g kg⁻¹ h⁻¹, respectively. Gas chromatograph (GC) analysis of FT synthesis products recovered from the reactor after reaction showed that chain growth probability (α) was 0.89. The FT synthesis reactivity for the bench-scale reaction was greater than that for the lab-scale reaction over the CoMnZr/SiO₂ catalyst. Therefore, the CoMnZr/SiO₂ catalyst can be adapted to the industrial process.

4.3. Hydrocracking of FT Products to Jet Fuel

To reduce CO₂ emissions from airplanes, extensive research and development of bio-aviation fuel to replace the present jet fuel obtained from fossil resources¹¹,₂². Jet fuel consists of a mixture of hydrocarbons with carbon numbers of 9-15 and is usually produced by distillation of crude oil, followed by hydrotreating and hydrocracking. Technologies to produce jet fuel from the BTL process are promising.

Unlike products from the hydrocracking of petroleum, the product from the BTL process does not include sulfur compounds. The presence of sulfur as a contaminant of liquid fuels is very undesirable. Ni-Co catalyst modified with heteropoly acid exhibits superior catalytic activity without sulfur treatment²³. We have investigated the effect of heteropoly acid promotion on Ni and/or Co supported zeolite catalysts for obtaining better hydrocracking activity.

Hydrocracking activities of oxide supported Ni + Co catalyst were examined. Hydrocracking reactivity was strongly influenced by the catalyst support. Ni + Co/SiO₂ catalyst exhibited much lower hydrocracking reactivity than Ni + Co/Al₂O₃ and Ni + Co/940HOA. Ni + Co/SiO₂ catalysts are obviously less acidic compared with Ni + Co/Al₂O₃ and Ni + Co/940HOA. Therefore, the acid properties of the catalyst may affect the catalytic behavior and 940HOA is a promising support for hydrocracking catalyst.

Comparison of H₃PW₁₂O₄₀/Ni(2.5) + Co(0.5)/940HOA and Ni(2.5) + Co(0.5)/940HOA found the former achieved higher yield of the corresponding jet fuel (Yₙ₋₁₅) and Y₁₋₈ (Fig. 11). Addition of H₃PW₁₂O₄₀ to Ni + Co/940HOA enhanced the hydrocracking activity. Delayed impregnation of Ni + Co/940HOA with H₃PW₁₂O₄₀ resulted in greater suppression of excess cracking. As a result, H₃PW₁₂O₄₀/Ni(2.5) + Co(0.5)/940HOA exhibited the highest Yₙ₋₁₅ and the lowest Y₁₋₈. The results were superior to those of both Ni and Co individually impregnated catalyst.

To enhance the performance, H₃PW₁₂O₄₀/Ni + Co/940HOA catalysts with different H₃PW₁₂O₄₀ to 940HOA ratios were investigated. The optimum H₃PW₁₂O₄₀ to 940HOA ratio for Yₙ₋₁₅ was obtained at 0.5. The NH₃-temperature-programmed desorption (TPD) results indicated that high H₃PW₁₂O₄₀ to 940HOA ratio enhanced the strong acid sites and this was related to the improved hydrocracking reactivity of the catalyst. Moderate H₃PW₁₂O₄₀ to 940HOA ratio catalyst with well-balanced acid amount and strength exhibited the optimum catalytic activity for hydrocracking of hexatriacontane. H₃PW₁₂O₄₀/Ni + Co/940HOA catalyst also exhibited 26.7% yield of Yₙ₋₁₅ in the hydrocracking of the biomass-derived FT synthesis products. H₃PW₁₂O₄₀/Ni + Co/940HOA catalyst may represent an...
gas composition for bio-DME synthesis was 39.8% H2, using a bench-scale BTL plant. The final compressed BTL process for bio-DME production is very promising. We have developed and adapted the synthesis of DME from woody biomass via gasification DME synthesis catalyst (Cu-Zn/γ-Al2O3) for methanol synthesis) and γ-Al2O3 (for methanol dehydration) was used as the DME synthesis catalyst (Cu-Zn/γ-Al2O3 = 1). Bench-scale DME synthesis was also conducted using a 2.4 L volume fixed bed reactor with 500 g of catalyzed at 0.98 MPa.

The results of extended DME production are shown in Fig. 12. DME concentration of around 16 vol% of the product gas was obtained under the following conditions: 0.98 MPa, 230 °C, W/F = 75.8 cat.-kg h/m3. Almost all DME in the gas phase could be recovered using the activated carbon trap with 233 K cooling. Finally, continuous synthesis of DME for over 600 h was achieved and approximately 1.1 kg of liquefied bio-DME recovered.

The bio-DME was used for the DME vehicle running test performed by the DME Vehicle Promotion Committee (DMEVPC).

5. Conclusion

Power generation based on effective utilization of biomass is being commercialized under a subsidy system such as the Feed-in Tariff (FIT) policy in Japan. However, several problems have been pointed out with the FIT system and conversion to other liquid fuels and raw materials for chemical products, so the hurdles to large-scale commercialization are still high due to cost problems.

Investigations of development of catalytic biomass conversion both on the laboratory scale and bench scale are reported here. No process has reached final commercialization. However, the importance of biomass utilization will increase in the future low-carbon society, so we will continue to promote biomass conversion technology and we would like to continue our efforts towards social implementation of biomass utilization.

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要　旨
非可食・未利用バイオマスの触媒変換によるガス化と液体燃料製造に関する研究

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バイオマス利用においては、食料と競合しないバイオマスを原料とした利用技術の開発が求められる。一方で、木質バイオマスに代表されるリグノセルロース系バイオマスは特にリグニン分などに由来するその強固な化学構造が化成品原料への変換の障害となる。筆者らは触媒反応を用いることで、種々のバイオマスから各種の燃料や化学物質を効率的に製造する様々な技術の開発・実証に取り組んできた。ラボスケールでの研究に加え、スケールアップした反応系としてバイオマスのガス化から液体燃料製造までの一貫したプロセス開発に取り組み、一貫型BTL（biomass to liquid fuel）ベンチプラントの安定的な実証運転による液体燃料製造を実現し、また実バイオマスを原料としたバイオジェンールエーテル（DME）の製造を行い、バイオDME混合燃料による実車走行試験への提供などを行ってきた結果を報告する。

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