Article

Selective Synthesis of Gasoline-Ranged Hydrocarbons from Syngas over Hybrid Catalyst Consisting of Metal-Loaded ZSM-5 Coupled with Copper-Zinc Oxide

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Abstract: The conversion of syngas ($CO + H_2$) to gasoline-ranged hydrocarbons was carried out using a hybrid catalyst consisting of metal-loaded ZSM-5 coupled with Cu-ZnO in a near-critical *n*-hexane solvent. Methanol was synthesized from syngas over Cu-ZnO; subsequently, was converted to hydrocarbons through the formation of dimethyl ether (DME) over the metal-loaded ZSM-5. When 0.5 wt% Pd/ZSM-5 and 5 wt% Cu/ZSM-5 among the metal-loaded ZSM-5 catalysts with Pd, Co, Fe or Cu were employed as a portion of the hybrid catalyst, the gasoline-ranged hydrocarbons were selectively produced (the gasoline-ranged hydrocarbons in all hydrocarbons: 59% for the hybrid catalyst with Pd/ZSM-5 and 64% for that with Cu/ZSM-5) with a similar CO conversion during the reaction. An increase in the Cu loading on ZSM-5 resulted in increasing the yield of the gasoline-ranged hydrocarbons, and in decreasing the yield of DME. Furthermore, the hybrid catalyst with Cu/ZSM-5 exhibited no deactivation for 30 h of the reaction. It was revealed that a hybrid catalyst containing Cu/ZSM-5 was efficient in the selective synthesis of gasoline-ranged hydrocarbons from syngas via methanol in the near-critical *n*-hexane fluid.

Keywords: hybrid catalyst; metal-loaded ZSM-5; syngas; near-critical phase; gasoline; methanol-to-hydrocarbons; copper-zinc oxide; Cu species

1. Introduction

Accompanying an increase in worldwide energy consumption, demands for specified liquid fuels such as gasoline, jet fuel and diesel fuel have highly increased. The Gas-to-Liquid (GTL) system has been focused on as a production process of hydrocarbons for liquefied fuels using natural gas as a carbon resource alternative to crude oil. In the GTL process, natural gas is first converted to syngas, which consists of carbon monoxide and hydrogen. Syngas can be converted directly to hydrocarbons through the Fischer-Tropsch synthesis (FTS) using metal-based catalysts [1–6]. Another means of hydrocarbon production from syngas is a two-stage process: (1) the conversion of syngas to methanol over metal-based catalysts; (2) the conversion of methanol to hydrocarbons through the Methanol-to-Hydrocarbons (MTH) reaction over solid acid catalysts [7,8]. In the MTH reaction, hydrocarbon distribution is strongly influenced by the micropore size of zeolites as an acid catalyst [8–11]. Thus, it is expected that by employing zeolites with optimal pore sizes, the process through the MTH reaction is capable of the selective production of hydrocarbons from syngas. Among zeolites, ZSM-5 with the **MFI** structure has been recognized as a prime candidate for the MTH reaction because of its pore size, which is suitable for the synthesis of gasoline-ranged hydrocarbons as well as high resistance to a deactivation [8–10].

A one-step process of the synthesis of saturated hydrocarbons in liquefied petroleum gas (LPG) fraction from syngas was achieved by employing hybrid catalysts composed of a methanol synthesis catalyst, e.g., Cu-ZnO and Cr-ZnO, and a metal-loaded zeolite catalyst [12–14]. In these processes, methanol generated from syngas can be rapidly converted to hydrocarbons because the zeolite catalyst is placed close to the methanol synthesis catalyst. The rapid consumption of methanol leads to higher yield of hydrocarbons than the calculated value based on the thermodynamic equilibrium [12]. Moreover, metal species with hydrogenation ability, such as Pd and Pt, supported on a zeolite effectively converts olefins, which are primarily generated in the MTH reaction, to paraffins under conditions of hydrogen existing. In addition, the hydrogenation by the metal species is expected to decompose carbonaceous species to suppress the deposition of heavy coke in/on the zeolite, leading to longevity of the catalyst. Recently, we have reported that the hybrid catalyst consisting of Cu-ZnO coupled with Pd/ZSM-5 exhibited a slow deactivation with a comparative yield of gasoline-ranged hydrocarbons compared with the hybrid catalyst with H-ZSM-5 in the conversion of syngas to hydrocarbons through the formation of methanol [15].

It has been accepted that loading metal species on zeolite not only provides a metal-acid bifunction for a catalyst but induces synergetic effects due to interactions between metal species and acid sites of zeolite. Conte *et al.* have reported that in the methanol conversion, the selectivity to aromatic compounds was improved by loading metal species on ZSM-5 due to the interaction of acid sites of zeolite with basic sites of metal oxide [16]. The interaction of metal species with acid sites of zeolite involves changes in acid properties of the zeolite as well. The acid strength of ZSM-5 was weakened by the introduction of transition metal species on the surface of ZSM-5, leading to inhibiting undesirable reactions such as the cracking of hydrocarbon products [17]. Furthermore, it has been proposed that hydrogen dissociated on metal species moves onto the surface of a zeolite support to generate active sites [18,19]. The synergetic effects are strongly dependent on loaded metal species.

Thus, it occurs to us to apply metal-loaded ZSM-5 catalysts to the development of a hybrid catalyst for the selective synthesis of gasoline-ranged hydrocarbons from syngas.

We have previously reported that a near-critical *n*-hexane solvent improved the yield of hydrocarbons in the syngas conversion to hydrocarbons via methanol over the hybrid catalyst consisting of Cu-ZnO and the Pd-loaded zeolite because of a good heat transfer in the reaction system under the near-critical solvent flowing [15,20]. In this study, we investigated the catalytic activity of hybrid catalysts composed of Cu-ZnO and metal-loaded ZSM-5 in a near-critical *n*-hexane solvent in the conversion of syngas to hydrocarbons via methanol. Since low-cost sources are desirable for the preparation of catalysts, copper, cobalt and iron, which are non-precious metals, were employed for the preparation of metal-loaded ZSM-5 to compare their catalytic properties with those of Pd/ZSM-5. We also investigated the effects of the metal loading on the hydrocarbon formation, in particularly gasoline-ranged hydrocarbons yield, as well as the durability during the reaction.

2. Results and Discussion

Saturated hydrocarbons are produced from syngas over a hybrid catalyst consisting of Cu-ZnO and a metal-loaded ZSM-5 as follows: (1) the conversion of syngas to methanol over Cu-ZnO; (2) the subsequent conversion of the generated methanol to hydrocarbons through the formation of dimethyl ether (DME) over the acid sites of ZSM-5; and (3) the hydrogenation of primarily produced unsaturated hydrocarbons to saturated hydrocarbons over metal species on ZSM-5.

2.1. Hydrocarbon Synthesis from Syngas over Hybrid Catalyst Consisting of Cu-ZnO and Metal-Loaded ZSM-5

The catalytic properties of a hybrid catalyst consisting of Cu-ZnO and metal-loaded ZSM-5 were investigated in the conversion of syngas to hydrocarbons in a near-critical *n*-hexane solvent. The metal-loaded ZSM-5 catalysts were prepared by loading 0.5 wt% Pd, 5 wt% Fe, 5 wt% Co or 5 wt% Cu on ZSM-5 with the SiO_2/Al_2O_3 ratio of 23. Figure 1 shows product yields after 6.5 h of the reaction at 543 K. Except for the hybrid catalyst with Co/ZSM-5, each catalyst exhibited almost the same yield of the sum of hydrocarbons and DME. Hydrocarbons and DME are produced through the formation of methanol, indicating that the conversion of methanol to DME followed by hydrocarbons is independent of metal species. Pd/ZSM-5 produced selectively hydrocarbons in the gasoline fractions (C_5–C_9 saturated hydrocarbons) among the hydrocarbons with a high CO conversion of 67%. When Fe/ZSM-5 was employed as a portion of the hybrid catalyst, the CO conversion as well as the hydrocarbons yield was smaller than those of the other metal-loaded ZSM-5 catalysts, while DME was selectively produced. Thus, the conversion of DME to hydrocarbons did not take place smoothly over the Fe/ZSM-5 catalyst, resulting in decreasing the hydrocarbons yield. In addition, the yield of CO_2 generated through the water-gas-shift (WGS) reaction was decreased due to a decrease in H_2O generated through the conversion of DME to hydrocarbons. By contrast, the hybrid catalyst with Co/ZSM-5 gave the highest CO conversion as well as the hydrocarbons yield among the four hybrid catalysts. Among the hydrocarbons, methane in hydrocarbons in dry gas fraction was dominantly produced with the yield of 38%. In the conversion of methanol to hydrocarbons, hydrocarbons with a carbon number of more than 1 are dominantly produced as a result of the cracking of

intermediates [9,10]. These results indicated that the Co species on ZSM-5 caused selectively the methanation of CO, CO_2 and methanol under the present conditions. The hybrid catalyst with 5 wt% Cu/ZSM-5 showed the CO conversion of 64% and the 28% yield of hydrocarbons in the gasoline fraction, which were very similar to those over that with 0.5 wt% Pd/ZSM-5. The TOFs in terms of the carbon amount (C-mol) of hydrocarbon products per mole of the metal species were estimated to 478 h^{-1} and 8521 h^{-1} for 5 wt% Cu/ZSM-5 and 0.5 wt% Pd/ZSM-5, respectively. Although the TOFs were much different between the two catalysts, the hydrocarbon distributions were almost the same. Thus, the hydrocarbon formation from methanol or DME would be dependent on the acidity of ZSM-5, and 5 wt% Cu on ZSM-5 would have almost the same catalytic properties for the WGS reaction and the methanation as those of 0.5 wt% Pd on ZSM-5.

Figure 1. Product yield resulting from conversion of syngas to hydrocarbons over hybrid catalysts consisting of Cu-ZnO and metal-loaded ZSM-5. Reaction conditions: catalyst, 1.0 g (0.5 g Cu-ZnO and 0.5 g metal-loaded ZSM-5); temperature, 543 K; P_{syngas} = 2.5 MPa; $P_{n\text{-hexane}}$ = 1.5 MPa; W/F_{syngas} = 9.7 $g_{\text{-catalyst}}$ h mol^{-1}; H_2/CO = 1.9.
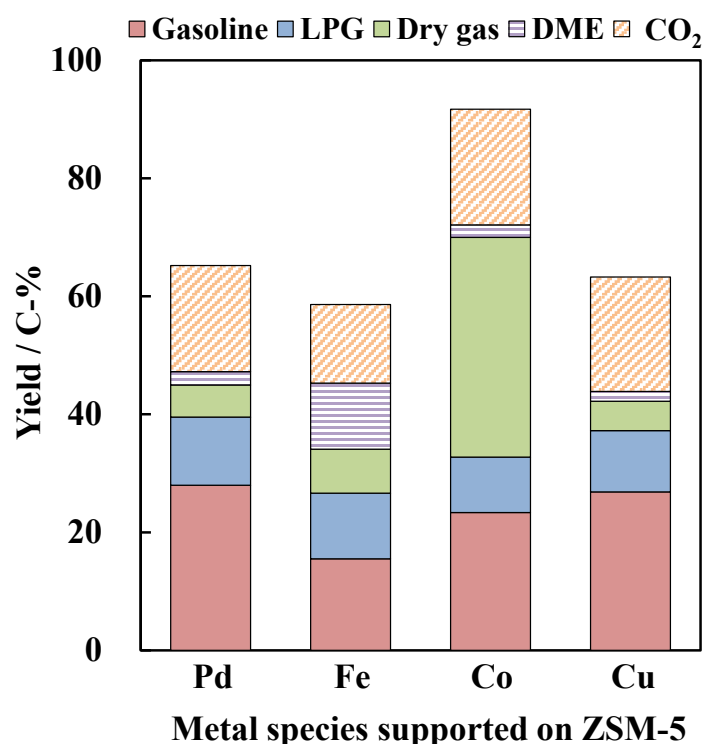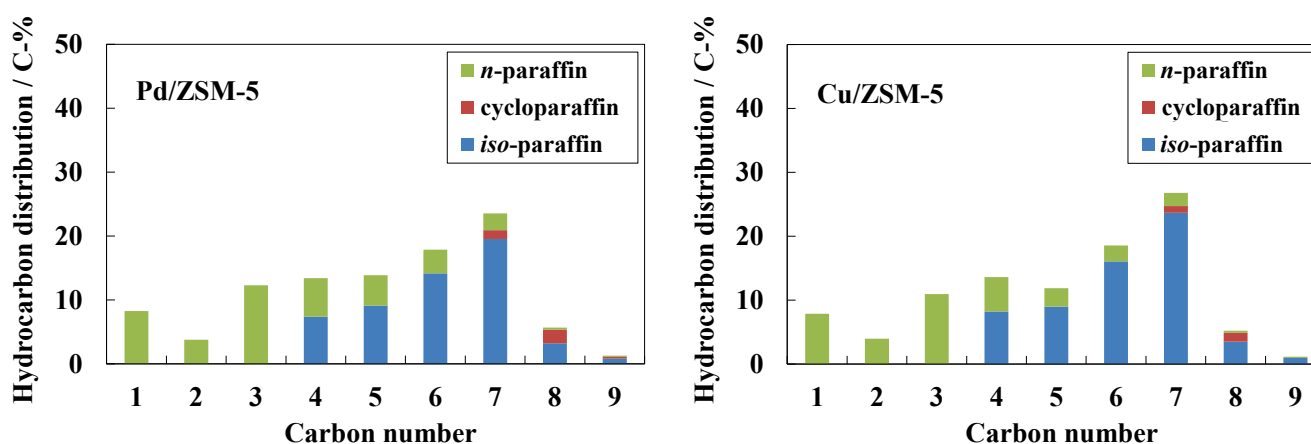

Figure 2 shows hydrocarbon distributions over the hybrid catalysts with 0.5 wt% Pd/ZSM-5 or 5 wt% Cu/ZSM-5. Both catalysts exhibited almost the same hydrocarbon distributions, and C_7 hydrocarbons were selectively produced. Only saturated hydrocarbons with a carbon number of less than 10 were obtained as products during the reaction. Among the gasoline-ranged hydrocarbons, the formation of *iso*-paraffins was more favorable than *n*-paraffins probably due to the isomerization of produced hydrocarbons over acid sites of ZSM-5. Furthermore, mono-branched paraffins such as 2-methylhexane and 3-methylpentane were mainly obtained as *iso*-paraffins. The carbon ratios of (*iso*-paraffins + cycloparaffins)/*n*-paraffins were 4.6 and 7.2 for 0.5 wt% Pd/ZSM-5 and 5 wt% Cu/ZSM-5, respectively. Metal species such as Pt and Pd, with a high hydrogenation ability, coexisting

with a solid acid catalyst supplies dissociated hydrogen species to the surface of the solid acid catalyst to generate active acid sites, which play an important role in the isomerization of alkane [18,19,21–24]. The amount of the Cu species on ZSM-5 was larger than that of the Pd species on ZSM-5. Thus, it is suggested that in the case of the hybrid catalyst with Cu/ZSM-5 the larger number of acid sites were generated from hydrogen dissociated on the metal species to cause the isomerization of hydrocarbon products without the cracking of hydrocarbons.

Figure 2. Hydrocarbon distribution resulting from conversion of syngas to hydrocarbons over hybrid catalysts with 0.5 wt% Pd/ZSM-5 or 5 wt% Cu/ZSM-5. Reaction conditions: catalyst, 1.0 g (0.5 g Cu-ZnO and 0.5 g metal-loaded ZSM-5); temperature, 543 K; P_{syngas} = 2.5 MPa; $P_{n\text{-}hexane}$ = 1.5 MPa; W/F_{syngas} = 9.7 $g_{\text{-catalyst}}$ h mol^{-1}; H_2/CO = 1.9.
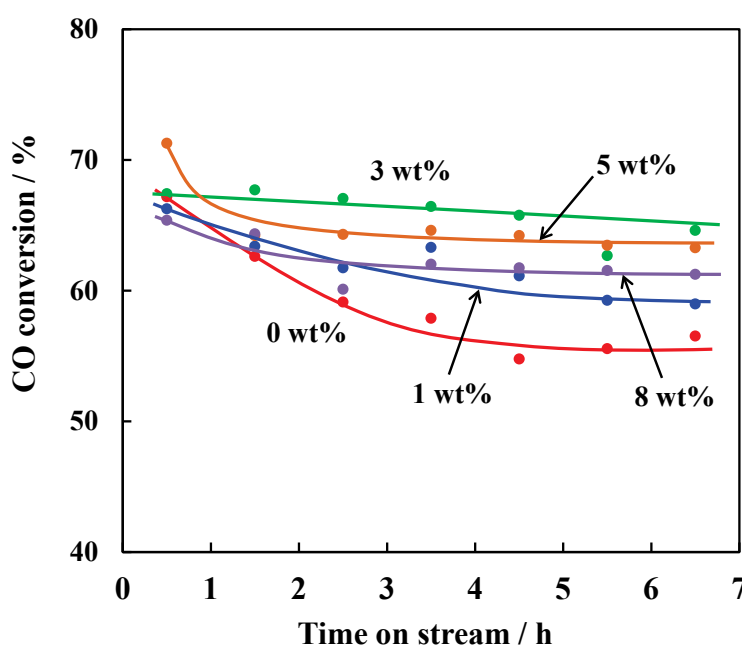

2.2. Effect of Copper Loaded on ZSM-5 on Catalytic Properties

The hydrogenation ability of the Cu species on ZSM-5 would play an important role in supplying acidic species to the surface of ZSM-5 as well as in hydrogenating olefins, which were primarily produced from DME, to paraffins. In addition, the hydrogenation ability is important to decompose carbonaceous species deposited in/on ZSM-5 because a rapid deactivation occurs due to the deposition of coke resulting from the further oligomerization of the carbonaceous species to cover the acid sites and/or to block the pores of the zeolite [25]. In order to investigate the effects of the Cu species on ZSM-5 on the durability of the catalyst, the conversion of syngas to hydrocarbons was conducted over the hybrid catalysts with the different Cu loadings on ZSM-5. Figure 3 shows time course plots of the CO conversions over the hybrid catalysts containing Cu/ZSM-5 with the different Cu loadings. The initial CO conversion was reached to ca. 67%, independent of the Cu loadings, indicating that the Cu species on ZSM-5 did not influence the conversion of syngas to methanol followed by DME. In the case of employing ZSM-5 without the Cu species, the CO conversion rapidly decreased after the reaction started until the conversion reached to 57% after 6.5 h. By loading even small amount of the Cu species on ZSM-5, the deactivation became slow. When 3 wt% Cu species was loaded on ZSM-5, the rapid deactivation was obviously suppressed compared with 0 wt% and 1 wt% Cu/ZSM-5, resulting in the CO conversion of 65% after 6.5 h of the reaction time. The inhibition of the deactivation by loading the Cu species on ZSM-5 is consistent with the previous report employing hybrid catalysts with Pd/ZSM-5 [15,20]. By contrast, a further increase in the Cu loading caused the

deactivation at the initial periods of the reaction again; in addition, decreased the CO conversion. However, the CO conversions of the hybrid catalysts with 5 wt% or 8 wt% Cu/ZSM-5 became constant after 2.5 h of the reaction time, while the slight deactivation was observed over the hybrid catalyst with 3 wt% Cu/ZSM-5 during the reaction.
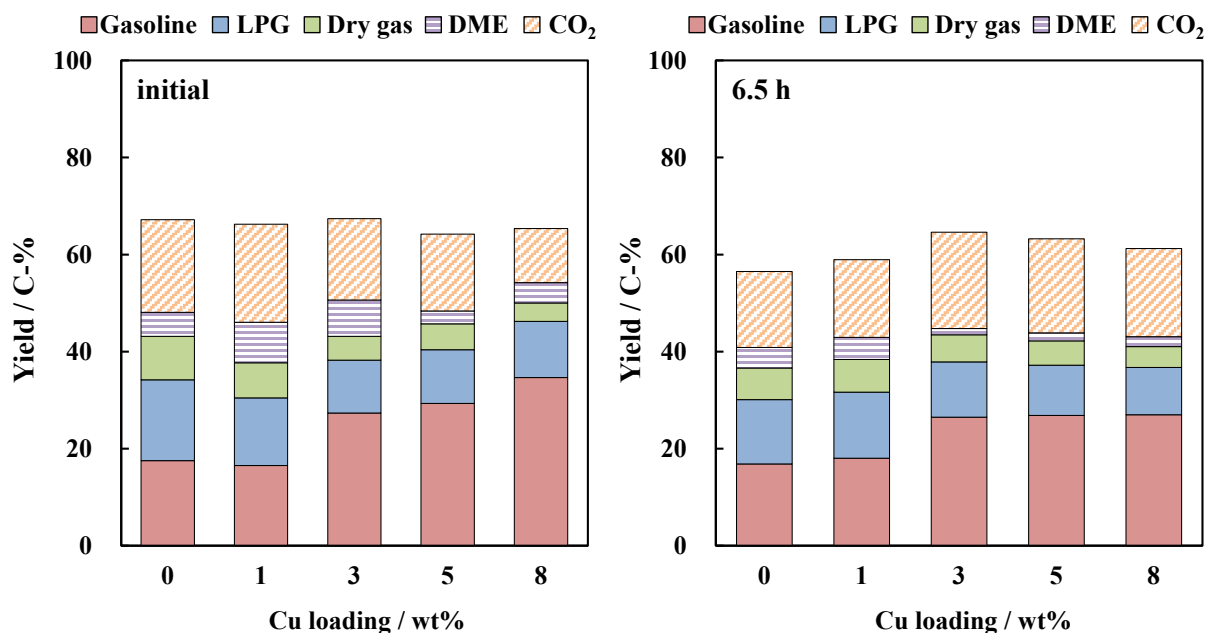
Figure 3. CO conversion over hybrid catalysts composed of Cu-ZnO and Cu/ZSM-5 with different Cu loading amounts. Reaction conditions: catalyst, 1.0 g (0.5 g Cu-ZnO and 0.5 g Cu/ZSM-5); temperature, 543 K; P_{syngas} = 2.5 MPa; $P_{n\text{-hexane}}$ = 1.5 MPa; W/F$_{syngas}$ = 9.7 g$_{\text{-catalyst}}$ h mol^{-1}; H_2/CO = 1.9.

Hydrogen uptakes determined from the hydrogen chemisorption measurement were 2.4 μmol g^{-1}, 3.6 μmol g^{-1}, and 3.6 μmol g^{-1} for 1 wt%, 5 wt%, and 8 wt% Cu/ZSM-5, respectively. The hydrogen uptake was increased by increasing the Cu loading. Thus, it is assumed that the Cu species on ZSM-5 inhibited the formation of heavy coke through the hydrogenation of carbonaceous species, leading to the suppression of the deactivation.

Figure 4 shows product yields at the initial period and after 6.5 h of the reaction at 543 K. In order to investigate the product distribution without the influence of the deactivation, the product yields at the initial period of the reaction were compared on the basis of a similar CO conversion. At the initial period, although the hydrocarbon yield of the hybrid catalyst with 1 wt% Cu/ZSM-5 was smaller than that of the hybrid catalyst with H-ZSM-5, the gasoline-ranged hydrocarbon yields of both the catalysts were almost the same values. Increasing the Cu loading resulted in an obvious increase in the gasoline-ranged hydrocarbons yield with the yields of hydrocarbons in LPG and dry gas fractions unchanged. Since CO_2 is generated from CO through the WGS reaction, a high hydrocarbon yield leads to the generation of a large amount of H_2O to encourage the CO_2 production through the WGS reaction. However, the CO_2 yield was decreased by increasing the Cu loading. It is indicated that the Cu species on ZSM-5 had less influence on the WGS reaction under the present conditions.

Figure 4. Product yield resulting from conversion of syngas to hydrocarbons over hybrid catalysts with Cu/ZSM-5 with different Cu loadings. Reaction conditions: catalyst, 1.0 g (0.5 g Cu-ZnO and 0.5 g Cu/ZSM-5); temperature, 543 K; P_{syngas} = 2.5 MPa; $P_{n\text{-hexane}}$ = 1.5 MPa; W/F_{syngas} = 9.7 g$_{\text{-catalyst}}$ h mol^{-1}; H_2/CO = 1.9.
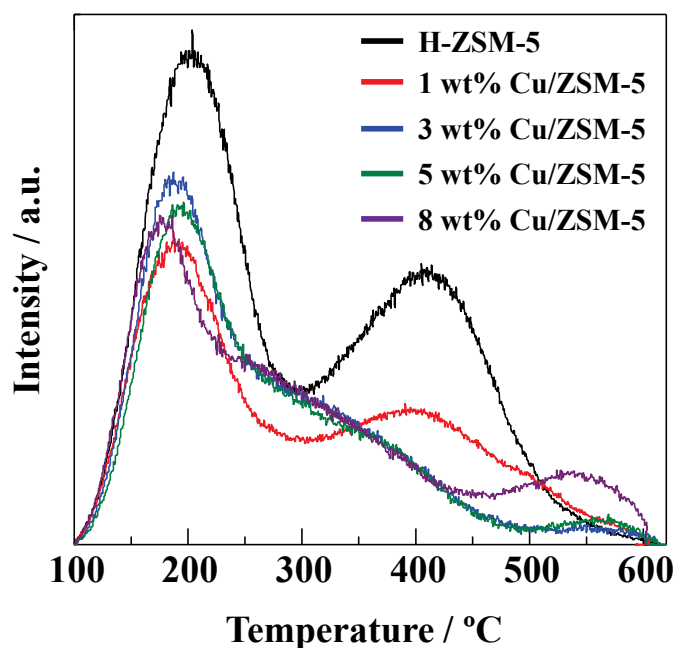

At 6.5 h after the reaction started, the product distribution was dependent on the Cu loading as well. An increase in the Cu loading resulted in increasing the gasoline-ranged hydrocarbons yield and in decreasing the DME yield. When increasing the Cu loading amount up to 5 wt%, the hydrocarbons yield slightly decreased with the slight increase in the gasoline-ranged hydrocarbons yield. It is implied that the Cu species on ZSM-5 would cover the acid sites causing the cracking of hydrocarbons, leading to the improvement in the yield of the gasoline-ranged hydrocarbons.

Acid sites of a catalyst should play an important role in the conversion of methanol to DME followed by hydrocarbons. Figure 5 shows NH_3-TPD profiles of Cu/ZSM-5 with the different Cu loadings. The acid amounts estimated from the peak at higher temperature were 0.99 mmol g^{-1}, 0.63 mmol g^{-1}, 0.52 mmol g^{-1}, 0.48 mmol g^{-1}, and 0.59 mmol g^{-1} for H-ZSM-5, 1 wt%, 3 wt%, 5 wt%, and 8 wt% Cu/ZSM-5, respectively. The peak at higher temperature was decreased by increasing the Cu loading. When the Cu loading was increased up to 3 wt%, a shoulder peak appeared at around 300 K. The peak at higher temperature (573–873 K) corresponds to NH_3 desorption from catalytically active acid sites [26,27]. It is suggested that the Cu species interacted with the acid sites of ZSM-5 to make their acid strength weaker. The high Cu loading (3–8 wt%) catalysts exhibited a new peak at around 550 K, and the peak was increased by increasing the Cu loading. Since the large peak was observed on Cu/ZSM-5 with the high Cu loading of 8 wt%, the peak can be derived from NH_3 adsorbed on the Cu species, which is consistent with the previous reports [28–30]. As shown in Figure 4, the gasoline-ranged hydrocarbons yield was drastically improved when the Cu loading was increased up to 3 wt%, while the slight increase in the gasoline-ranged hydrocarbons yield was observed by the further increase in the Cu loading, which was in line with the changes in the peak at the higher temperature in the NH_3-TPD profiles. Therefore, it is suggested that the weak acid sites generated by loading the Cu

species on ZSM-5 played an important role in the selective synthesis of the gasoline-ranged hydrocarbons without the polymerization and cracking of products because of mild acid strength.
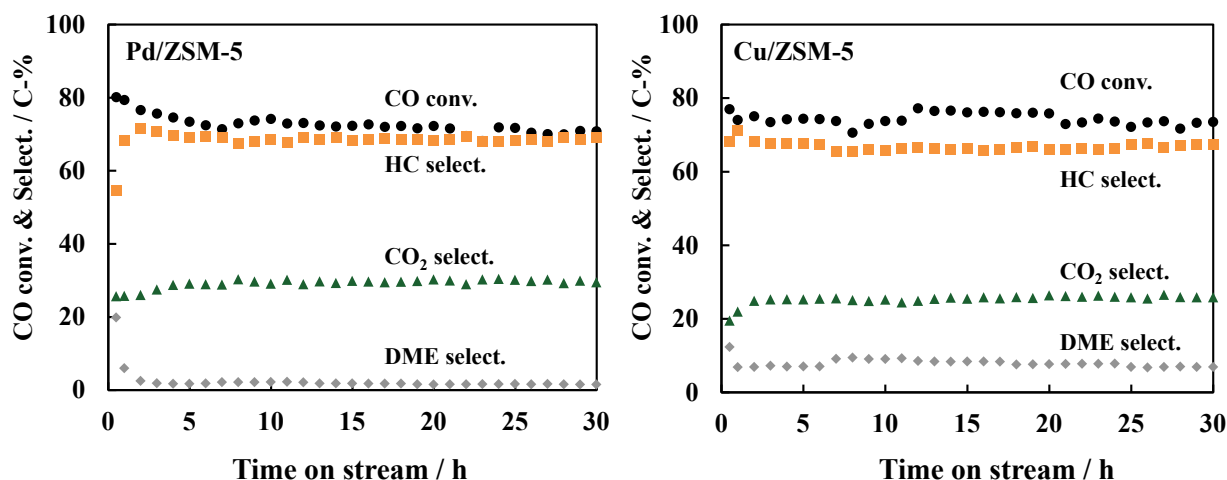
Figure 5. Temperature programmed ammonia desorption (NH_3-TPD) profiles of Cu/ZSM-5 with different Cu loading amounts.

2.3. Durability of Hybrid Catalyst with Cu/ZSM-5

In order to investigate the durability of the hybrid catalyst with Cu/ZSM-5 in the syngas conversion, the changes in the CO conversion and product selectivities along with time-on-stream were examined in a long-run reaction at 553 K. It is reported that by loading Pd on ZSM-5, a high CO conversion was retained without the rapid deactivation and changes in product distributions in the conversion of syngas to the gasoline-ranged hydrocarbons [15]. As shown in Figure 6, the initial CO conversion of the hybrid catalyst with 0.5 wt% Pd/ZSM-5 reached to 80%, while the hybrid catalyst with 5 wt% Cu/ZSM-5 exhibited 77% initial CO conversion. In the case of the hybrid catalyst with Pd/ZSM-5, the CO conversion gradually decreased until around 7 h after the reaction started, and then, the conversion of *ca.* 70% was kept until 30 h of the reaction time. By contrast, the CO conversion of the hybrid catalyst with Cu/ZSM-5 was kept constant with the value of *ca.* 74% during the reaction. Although CO_2 selectivity of the hybrid catalyst with Cu/ZSM-5 was slightly smaller than that of the hybrid catalyst with Pd/ZSM-5, the hybrid catalyst with Cu/ZSM-5 exhibited the higher DME selectivity than the hybrid catalyst with Pd/ZSM-5 during the reaction. These findings indicate that Cu/ZSM-5 constantly transformed methanol generated from syngas into DME followed by hydrocarbons without the rapid deposition of carbonaceous species on the catalyst during the reaction. Furthermore, the Cu species on ZSM-5 did not encourage the CO consumption through the WGS reaction compared with Pd/ZSM-5. Owing to the advantages mentioned above, Cu species is promising for the development of bifunctional catalysts in the selective synthesis of hydrocarbons from syngas, instead of precious metals such as Pd and Pt.

Figure 6. Conversion of syngas to hydrocarbons over hybrid catalysts with 0.5 wt% Pd/ZSM-5 and 5 wt% Cu/ZSM-5. Reaction conditions: catalyst, 1.0 g (0.5g Cu-ZnO and 0.5 g metal-loaded ZSM-5); temperature, 553 K; P_{syngas} = 2.5 MPa; $P_{n\text{-hexane}}$ = 1.5 MPa; W/F_{syngas} = 9.7 g-catalyst h mol^{-1}; H_2/CO = 1.9.

3. Experimental Section

3.1. Catalyst Preparation

Cu-ZnO was a commercial catalyst (MK-121, TOPSØE, Copenhagen, Denmark). Metal-loaded ZSM-5 catalysts were prepared by impregnation method with a metal salt aqueous solution and commercial ZSM-5 containing the SiO_2/Al_2O_3 molar ratio of 23 (CBV2314, Zeolyst, Conshohocken, PA, USA). 4.557 wt% $Pd(NH_3)_2(NO_3)_2$ aqueous solution, $Fe(NO_3)_2 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ were employed for the preparation of each metal salt aqueous solution. The commercial NH_4^+-type ZSM-5 was calcined at 823 K for 3 h to become a proton-type ZSM-5. The proton-type ZSM-5 was immersed in a metal salt aqueous solution with a supported metal weight at room temperature overnight. The resultant was evaporated at 333 K, dried at 393 K for 3 h, and calcined at 823 K for 3 h.

A hybrid catalyst was prepared by physically mixing the 355–710 μm pellets of a Cu-ZnO methanol synthesis catalyst of 0.5 g with those of a metal-loaded ZSM-5 catalyst of 0.5 g.
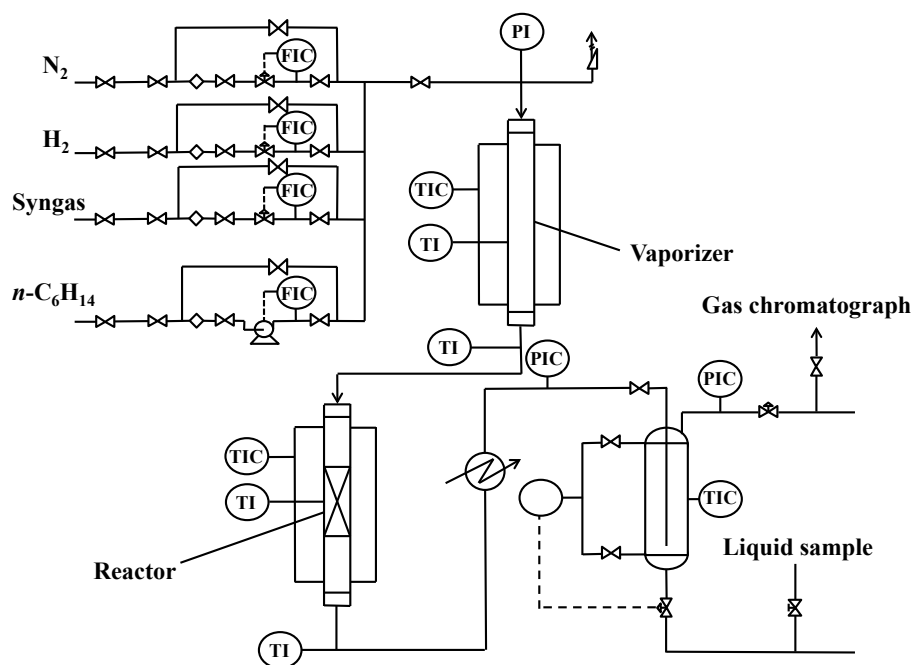
3.2. Characterization

Temperature programmed ammonia desorption (NH$_3$-TPD) profiles were recorded on a BELCAT instrument (BEL, Osaka, Japan). The sample was pretreated under a 10% H_2/He flow at 573 K for 3 h to make Cu on ZSM-5 reduced, and then cooled down to 373 K. Ammonia was allowed to make contact with the sample at 373 K for 30 min. Subsequently, the sample was evacuated to remove weakly adsorbed ammonia at 373 K for 15 min. Finally, the sample was heated from 373 K to 883 K at a raising rate of 10 K/min in a He flow (50 mL min^{-1}). A mass spectrometer was used to monitor desorbed NH$_3$ (m/e = 16). The amount of acid sites was determined by using the area in the profiles.

Hydrogen chemisorption measurements were carried out using an AS-1 adsorption instrument (Quantachrome Instrument Corp., Boynton Beach, FL, USA). The sample was pretreated under a H$_2$

flow at 673 K for 1 h to make Cu on ZSM-5 reduced, and then cooled down to 373 K. The measurements were conducted at 373 K to determine the uptake of hydrogen.

Figure 7. Scheme of experimental set-up. Abbreviations: FIC, Flow Indicator and Controller; PIC, Pressure Indicator and Controller; TIC, Temperature Indicator and Controller; PI, Pressure Indicator; TI, Temperature Indicator.

3.3. Catalytic Reaction Test

A pressurized flow type of reaction apparatus with a fixed-bed reactor was used for this study to carry out catalytic reaction tests following our previous reports [15,20]. The experimental set-up scheme is shown in Figure 7. A stainless tubular reactor with an inner diameter of 6 mm was employed. 1 g of a hybrid catalyst was loaded in the reactor, and inert glass sand was placed above and below the catalyst. The length of the catalyst bed was about 6.0–6.5 cm. The catalyst was reduced in a flow of a mixture of 5% hydrogen and 95% nitrogen with 100 mL min^{-1} at 573 K for 3 h, and then cooled down to 473 K. Syngas (60% H_2, 32% CO, 5% CO_2, and 3% Ar) and *n*-hexane as a solvent were introduced into the catalyst to make the total pressure inside reach to 4.0 MPa (P_{syngas}, 2.5 MPa; $P_{n\text{-hexane}}$, 1.5 MPa), and then the catalyst was heated up to 543 K. The catalyst weight to the flow rate ratio (W/F$_{syngas}$) was 9.7 g$_{-cat.}$ h mol^{-1}. CO, CO_2 and CH_4 of the reaction products were analyzed with an on-line gas chromatograph (Shimadzu, Kyoto, Japan; GC-8A) equipped with a thermal conductivity detector (TCD) and a packed column of activated charcoal. An Ar gas was contained in syngas as an internal standard gas. The light hydrocarbon products were analyzed with another on-line gas chromatograph (Shimadzu, Kyoto, Japan; GC-2014) equipped with a flame ionization detector (FID) and a capillary column of Porapak-Q. The products liquefied by condensation at room temperature were analyzed with an off-line gas chromatograph (Shimadzu, Kyoto, Japan; GC-2014) equipped with an FID detector and a capillary column of TC-1. For the analyses of the liquefied products, decahydronaphthalene (*n*-$C_{10}H_{18}$) was used as an internal standard.

3.4. Calculation Method

The conversion of CO was defined as

$$\text{CO conversion (\%)} = \left(1 - \frac{CO_{out}\ (mol)}{CO\ in\ feed\ (mol)} \right) \times 100 \tag{1}$$

The yield of C-containing products was defined based on the atomic carbon. The yield of CO_2 was defined as

$$CO_2\ \text{yield (C-\%)} = \frac{CO_2\ (mol)}{CO\ in\ feed\ (mol)} \times 100 \tag{2}$$

The yield of DME was defined as

$$\text{DME yield (C-\%)} = \frac{DME\ (mol) \times 2}{CO\ in\ feed\ (mol)} \times 100 \tag{3}$$

The yield of hydrocarbon was defined as

$$C_n\ \text{yield (C-\%)} = \frac{C_n\ (mol) \times n}{CO\ in\ feed\ (mol)} \times 100 \tag{4}$$

4. Conclusions

The catalytic performance of hybrid catalysts consisting of Cu-ZnO coupled with metal-loaded ZSM-5 have been studied in the syngas conversion to hydrocarbons via methanol in a near-critical *n*-hexane solvent. The hybrid catalyst consisting of 5 wt% Cu/ZSM-5 coupled with Cu-ZnO exhibited very similar catalytic performances to those over the hybrid catalyst containing 0.5 wt% Pd/ZSM-5, and produced selectively gasoline-ranged hydrocarbons from syngas. The Cu loaded on ZSM-5 influenced the deactivation rate as well as the product distribution. An increase in the Cu loading increased the gasoline-ranged hydrocarbons yield without the cracking of the products, and shortened time before the catalytic activity became stable with keeping a high CO conversion. The high Cu loading on ZSM-5 decreased the amount of the acid sites and weakened the acid strength of ZSM-5, which were estimated from NH_3-TPD profiles. These findings suggest that Cu species would interact with the acid sites of ZSM-5 to make the acid strength mild, leading to suppressing the excess polymerization and the cracking of products with keeping high ability of the methanol conversion to hydrocarbons. In addition, the Cu species on ZSM-5 exhibited less ability for the water-gas-shift reaction, resulting in the good catalytic stability without excess consumption of CO. Therefore, Cu/ZSM-5 as a portion of a hybrid catalyst is effective in the selective synthesis of the gasoline-ranged hydrocarbons from syngas.

Conflicts of Interest

The authors declare no conflict of interest.

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