Research Article

Synthesis of Hydrocarbons from H_2 -Deficient Syngas in Fischer-Tropsch Synthesis over Co-Based Catalyst Coupled with Fe-Based Catalyst as Water-Gas Shift Reaction

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Received 6 March 2015; Accepted 19 April 2015

Academic Editor: Hongmei Luo

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The effects of metal species in an Fe-based catalyst on structural properties were investigated through the synthesis of Fe-based catalysts containing various metal species such as Mn, Zr, and Ce. The addition of the metal species to the Fe-based catalyst resulted in high dispersions of the Fe species and high surface areas due to the formation of mesoporous voids about 2–4 nm surrounded by the catalyst particles. The metal-added Fe-based catalysts were employed together with Co-loaded beta zeolite for the synthesis of hydrocarbons from syngas with a lower H_2/CO ratio of 1 than the stoichiometric H_2/CO ratio of 2 for the Fischer-Tropsch synthesis (FTS). Among the catalysts, the Mn-added Fe-based catalyst exhibited a high activity for the water-gas shift (WGS) reaction with a comparative durability, leading to the enhancement of the CO hydrogenation in the FTS in comparison with Co-loaded beta zeolite alone. Furthermore, the loading of Pd on the Mn-added Fe-based catalyst enhanced the catalytic durability due to the hydrogenation of carbonaceous species by the hydrogen activated over Pd.

1. Introduction

The use of biomass materials as renewable resources has been focused on for the production of sustainable liquefied fuels as well as the fixation of emitted CO_2 [1, 2], the so-called “biomass-to-liquid (BTL) process.” In the BTL process, the gasification of biomass materials produces mainly syngas composed of carbon monoxide and hydrogen; subsequently, syngas can be directly converted to hydrocarbons as liquefied fuels such as diesel fuel through the Fischer-Tropsch synthesis (FTS) over Fe- and Co-based catalysts. Syngas obtained from biomass materials usually contains lower ratios of hydrogen to carbon monoxide than syngas derived from natural gas; the H_2/CO molecular ratio is below 2 [3, 4]. However, the H_2/CO ratio of 2 is required for the stoichiometric hydrogenation of carbon monoxide to hydrocarbons in the FTS; furthermore, the reaction rate in the FTS is positively dependent on the partial pressure of hydrogen [5–7]. Therefore, from the viewpoint of the efficient production of hydrocarbons from the H_2 -deficient syngas, methods for increasing the H_2/CO ratio during the FTS are highly desirable.

The water-gas shift (WGS) reaction is an important process for the production of hydrogen through the reaction of carbon monoxide with water. In the FTS, even if the steam is not introduced into a reaction system, water is produced through the CO hydrogenation. Thus, the use of a WGS catalyst together with an FTS catalyst can continuously supply hydrogen required for the FTS through the WGS reaction with generated water and a portion of CO in syngas. For the conversion of H_2 -deficient syngas to hydrocarbons, Fe-based catalysts have been attractive since Fe-based catalysts have high activities for both the WGS reaction and the FTS to attain an efficient utilization of carbon monoxide [8–13]. Furthermore, the catalytic activity of Fe-based catalysts can be promoted by the introduction of metal species such as Cu, Mn, Ce, and Zr to the catalysts because of the enhancement of the reducibility of Fe species ($Fe_2O_3 \rightarrow Fe_3O_4$) [14–17] as well as high dispersions of nanosized Fe crystallites [18–20]. However, in the FTS over the Fe-based catalyst, both the WGS reaction and the FTS can simultaneously proceed; meanwhile, carbonaceous species, which are formed in the carbon growth, are deposited on the catalyst to cause

the deactivation by the covering of active sites of the catalyst [13, 21, 22].

The combination of catalysts with different functions is expected to be effective in the construction of processes where different reactions occur simultaneously and/or sequentially. It has been reported that the selective synthesis of specific hydrocarbons from syngas was attained using an FTS catalyst together with a zeolite as an acid catalyst [23–25]. The FTS catalyst produced hydrocarbons from syngas, and the zeolite converted the produced hydrocarbons to specific hydrocarbons through the isomerization/cracking. In the synthesis of hydrocarbons through the formation of methanol, a methanol synthesis catalyst such as Cu-ZnO was employed together with a zeolite to show high catalytic activity [26–28]. In addition, the methanol synthesis catalyst was not covered with carbonaceous species which were deposited on the zeolite, leading to the improvement of the catalyst life. When a WGS catalyst is employed together with an FTS catalyst in the synthesis of hydrocarbons from H_2 -deficient syngas, it is expected that the FTS reaction would proceed more efficiently by increasing the hydrogen concentration through the WGS reaction in comparison with the FTS catalyst alone. Furthermore, the catalyst activity of the WGS catalyst would be retained because carbonaceous species which are deposited on the FTS catalyst cannot move to the WGS catalyst.

In the present study, we investigated the catalytic properties of hybrid catalysts composed of a catalyst for the WGS reaction and a catalyst for the FTS in the conversion of H_2 -deficient syngas to hydrocarbons. In particular, the catalytic activity of the WGS catalyst was focused on for the enhancement of the CO hydrogenation by the supply of hydrogen. Since Co-based catalysts have a higher activity for the CO hydrogenation than Fe-based catalysts [29], the Co-based catalyst and the Fe-based catalyst were employed as an FTS catalyst and a WGS catalyst, respectively. We also investigated the effect of the addition of metal species to the Fe-based WGS catalyst on the physicochemical and catalytic properties.

2. Experimental

2.1. WGS Catalyst Preparation. Metal-added Fe-based WGS catalysts, M-FeCu (M = Zr, Mn, and Ce), were prepared by the coprecipitation method using $Fe(NO_3)_3 \cdot 9H_2O$ (Kanto Chem. Co.), $Cu(NO_3)_2 \cdot 3H_2O$ (Kanto Chem. Co.), $ZrO(NO_3)_2 \cdot 2H_2O$ (Kanto Chem. Co.), $Mn(NO_3)_2 \cdot 6H_2O$ (Kanto Chem. Co.), and $Ce(NO_3)_3 \cdot 6H_2O$ (Kanto Chem. Co.) as Fe, Cu, Zr, Mn, and Ce sources, respectively. 2 M Na_2CO_3 aqueous solution was dropped into a mixed aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $M(NO_3)_x \cdot nH_2O$ to adjust a pH value of the solution at around 8 at 353 K. Continuously, the resultant gel was stirred at 353 K for 1 h. The obtained product was recovered by filtration, washed with hot deionized water to remove sodium cations, and dried at 393 K for 12 h. A KNO_3 aqueous solution was added to the product by impregnation method. The mixture was evaporated at 333 K, dried at 393 K for 3 h, and calcined at 673 K for 3 h.

The nominal weight ratio of the Fe-based catalyst was 100 Fe:1 Cu:2 K, and the added amount of M was 0 wt.%, 10 wt.%, and 20 wt.% on the basis of the weight of the Fe-based catalyst.

A Pd-modified WGS catalyst was prepared by impregnation method with 4.6 wt.% $Pd(NH_3)_2(NO_3)_2$ aqueous solution. The 10 wt.% Mn-containing FeCu catalyst was immersed in the aqueous solution with Pd for preparing 1 wt.% Pd-loaded Mn-FeCu 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.

2.2. FTS Catalyst Preparation. A Co supported on beta zeolite catalyst (Co/ β) with a nominal Co loading of 20 wt.% was applied as an FTS catalyst. Co/ β was prepared by impregnation method using $Co(NO_3)_2 \cdot 6H_2O$ (Kanto Chem. Co.) aqueous solution and commercial beta zeolite (CP814E, Zeolyst). Prior to the impregnation, commercial NH_4^+ -type beta zeolite was calcined at 823 K for 3 h to become proton-type beta zeolite. Proton-type beta zeolite was immersed in the $Co(NO_3)_2 \cdot 6H_2O$ aqueous solution at room temperature overnight. The resulting mixture was evaporated at 333 K, dried at 393 K for 3 h, and calcined at 573 K for 3 h.

2.3. Characterization. XRD patterns were collected on a SmartLab (Rigaku) instrument using a Cu-K α X-ray source (40 kV, 20 mA). Nitrogen adsorption-desorption measurements were conducted at 77 K on a BELSORP-mini II (MicrotracBEL Corp.) instrument. Prior to the measurement, the WGS catalyst was evacuated at 473 K for 2 h. The BET (Brunauer-Emmett-Teller) specific surface area was calculated from the adsorption data. The pore size distribution was estimated from the desorption data by BJH (Barrett-Joyner-Halenda) method. Field-emission scanning microscopic (FE-SEM) images of the samples were obtained on an S-5200 microscope (Hitachi) operating at 1.0–5.0 kV. The sample was mounted on a carbon-coated microgrid (Okensoji Co.) without any metal coating. Transmission electron microscope (TEM) images of the powder samples were obtained on a TEM instrument (JEOL) operating at 100–300 kV. Elemental analyses of the WGS catalyst were performed on a JXA-8100 electron probe microanalyzer (EPMA, JEOL) operating at 15 kV and a backscatter electronic beam diameter of 10 μm . Hydrogen temperature-programmed reduction (H_2 -TPR) profiles of the samples were recorded on a BELCAT (MicrotracBEL Corp.) apparatus. Typically, the sample was pretreated at 673 K in He (50 mL min^{-1}) for 1 h and then was cooled to 323 K. Then, the sample was heated up to 973 K at a ramping rate of 5 K min^{-1} with 10% H_2/He flow (30 mL min^{-1}) passed through the reactor. A mass spectrometer was used to monitor the water flow ($m/e = 18$) generated through the reduction of the sample by hydrogen.

2.4. Syngas Conversion to Hydrocarbons. A pressurized flow type of reaction apparatus with a fixed-bed reactor was used to carry out the conversion of syngas to hydrocarbons. A hybrid catalyst was obtained by physically mixing 0.5 g of

TABLE 1: Physicochemical properties of Fe-based samples.

Sample	S.A. _{BET} ^a (m ² g ⁻¹)	Pore volume ^a (cm ³ g ⁻¹)	Pore size ^a (nm)
FeCu	46	0.25	11
Zr-FeCu (10 wt.% Zr)	175	0.22	2.1
Zr-FeCu (20 wt.% Zr)	181	0.22	2.1
Mn-FeCu	183	0.25	2.1
Ce-FeCu	163	0.27	2.7

^aEstimated by N₂ adsorption-desorption method.

355–710 μm pellets of the WGS catalyst with 1.5 g of 355–710 μm pellets of the FTS catalyst. 2.0 g of the hybrid catalyst was centered in a stainless tubular reactor with an inner diameter of 6 mm. The length of the catalyst bed was about 13–14 cm. Prior to the reaction, the hybrid catalyst was reduced in a hydrogen flow of 50 mL min⁻¹ at 673 K for 3 h and then cooled down to room temperature. Syngas (48.5 vol.% H₂, 48.5 vol.% CO, and 3 vol.% Ar) was introduced into the catalyst bed to make the pressure inside reach 1.0 MPa, and then the catalyst was heated up to 513 K. The catalyst weight to the flow rate ratio (W/F_{syngas}) was 16.3 g_{cat} h mol⁻¹. CO, CO₂, and CH₄ in the outlet gas which passed through the catalyst bed were analyzed with an on-line gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) and a packed column of activated charcoal. The light hydrocarbons in the reaction products were analyzed with another on-line gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a capillary column of InertCap 1. The products liquefied by condensation at room temperature were analyzed with an off-line gas chromatograph (Shimadzu GC-2014) equipped with an FID detector and a capillary column of TC-1. For the analyses of the liquefied products, decahydronaphthalene (n-C₁₀H₁₈) was used as an internal standard.

3. Results and Discussion

3.1. Preparation of Metal-Added Fe-Based WGS Catalyst. XRD patterns of calcined conventional Fe-based WGS catalyst (FeCu) and metal-added Fe-based catalysts are shown in Figure 1. Calcined FeCu exhibited an XRD typical of hematite. When Zr, Mn, or Ce species was introduced to the FeCu sample during the coprecipitation, only broadened peaks were observed at around 35° and 63.5° without any discernable peaks attributed to metal and metal oxide phases. Even when the amount of the added Zr species was increased up to 20 wt.%, no change was observed in the XRD pattern; only broadened peaks appeared at around 35° and 63.5°. In the synthesis of Fe-based FTS catalysts, the introduction of metal species such as Cr, Mo, and Mn to the catalyst leads to the formation of small oxide crystallites less than 4–5 nm in size [18, 19]. These results suggest that the addition of the metal species to the Fe-based catalyst would promote the dispersion of the Fe species and the other metal species to form nanosized composites, independent of the added metal species.

FIGURE 1: XRD patterns of FeCu and metal-added Fe-based samples.

Figure 2 shows the N₂ adsorption-desorption isotherms and pore size distributions estimated by BJH method for the FeCu and metal-added Fe-based samples. All the samples showed a type IV isotherm, which is classified by IUPAC, with hysteresis. The FeCu sample exhibited the hysteresis at high relative pressures ($P/P_0 = 0.8–0.95$), which was derived from voids among the FeCu particles. By contrast, the hysteresis of the N₂ isotherms for the metal-added Fe-based samples appeared at $P/P_0 = 0.45–0.75$, regardless of the added metal species. In the pore size distribution, the metal-added Fe-based samples exhibited a peak in a range of diameters of mesopores (more than 2 nm), while no sharp peak was observed for the FeCu sample. Since Fe-based catalysts prepared by conventional coprecipitation method are not mesoporous materials, the peaks in the pore size distribution can be assigned to mesopore-like voids surrounded by nanosized particles of the Fe-based catalyst. The BET surface areas, pore volumes, and pore sizes of the calcined catalysts are summarized in Table 1. The BET surface area was drastically increased by the addition of the metal species to the Fe-based catalyst because of the formation of the mesoporous voids. Moreover, the BET surface area was independent of the added amount of the metal species;

FIGURE 2: N_2 adsorption and desorption isotherms (a) and pore size distributions (b) of FeCu and metal-added Fe-based samples.

FIGURE 3: FE-SEM images of (a) FeCu, (b, c) 10 wt.% Zr-FeCu, (d) Mn-FeCu, and (e, f) Ce-FeCu. Voids are indicated by white arrows.

the BET surface areas were found to be 175 and 181 $\text{m}^2 \text{g}^{-1}$ for 10 wt.% Zr-FeCu and 20 wt.% Zr-FeCu, respectively.

Figure 3 shows FE-SEM images of calcined FeCu and the metal-added Fe-based samples. FeCu was composed of small particles ca. 60 nm in size. On the other hand, the SEM images of the metal-added Fe-based samples showed

significantly large masses resulting from the agglomeration of small particles, regardless of the added metal species. The morphology of the metal-added Fe-based samples was also evaluated by TEM observations (Figure 4). It was found that particles ca. 4–5 nm in size were agglomerated to form large masses, independent of the added metal species. These

FIGURE 4: TEM images of (a) 10 wt.% Zr-FeCu, (b) Mn-FeCu, and (c) Ce-FeCu.

FIGURE 5: EPMA mapping images of (a) 10 wt.% Zr-FeCu, (b) Mn-FeCu, and (c) Ce-FeCu.

findings were consistent with the XRD findings. In addition, a number of voids were observed in the large agglomerates (Figures 3(c) and 3(f)), whose voids were in agreement with the mesoporous voids estimated by the N_2 adsorption measurement.

The elemental analyses of the metal-added Fe-based samples were conducted with EPMA (Figure 5). Homogeneous

dispersion of Fe species was observed on all the samples. Zr species and Ce species were homogeneously dispersed on the 10 wt.% Zr-FeCu and Ce-FeCu samples, respectively. These findings were consistent with the XRD findings. By contrast, the gatherings of Mn species were observed on the Mn-FeCu sample although Mn species were spread out on the sample. No peak derived from Fe-Mn composites or Mn oxides was

FIGURE 6: H_2 -TPR profiles of FeCu and metal-added Fe-based samples.

observed in the XRD pattern of Mn-FeCu, suggesting that crystalline agglomerations composed of Mn species were not formed even if Mn species were gathered in the sample.

The reducibility of the metal-added Fe-based catalysts was estimated from the H_2 -TPR profiles (Figure 6). The FeCu catalyst exhibited two peaks attributed to H_2O generated through the reduction by H_2 at around 600 and 900 K, which corresponds to H_2 -TPR profile observed in the two-step reduction of hematite, that is, $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$ [15, 30, 31], indicating that the first peak at lower temperature is ascribed to the reduction of Fe_2O_3 to Fe_3O_4 , and the second peak at higher temperature is ascribed to further reduction of Fe_3O_4 . The reduction of Fe species can be promoted by the addition of Cu species, leading to a shift of a peak attributed to the reduction of Fe_2O_3 to Fe_3O_4 to lower temperature in H_2 -TPR profiles [14–16], whereas K species suppresses the reduction of Fe and Cu species due to the interaction between the K species and the metal species [32, 33]. Thus, it is suggested that the reducibility of the Fe species may not be promoted in the FeCu catalyst due to the presence of the K species although the Cu species coexisted in the catalyst. All the metal-added Fe-based samples exhibited two peaks derived from the reduction of the Fe species at around 600 and 900 K, which was similar to the finding in H_2 -TPR of the FeCu sample. However, the first peak of all the metal-added Fe-based catalysts was shifted to higher temperatures in comparison with that of the FeCu sample. In addition, the temperature where the first peak appeared was slightly increased with an increase in the amount of added Zr. In an Fe-based FTS catalyst containing SiO_2 , the reducibility of Fe oxides is not influenced by the coexistence of Zr, regardless of the amount of Zr [18, 19]. By contrast, Qing et al. have reported that in the H_2 -TPR profiles a first peak of a calcined composite of Fe and Zr without SiO_2 appeared at higher

temperature than that of hematite due to the cover of Fe sites with enriched Zr [34]. The addition of Mn or Ce species to Fe-based catalysts causes the interaction between the Fe species and the metal species, leading to the delay of the reduction of the Fe species [20, 35–37]. According to the findings reported above, it is suggested that in the metal-added Fe-based catalysts the reduction of the Fe species was suppressed to shift the first peak to higher temperature in the H_2 -TPR profile due to the interaction of the Fe species and the metal species resulting from the addition of the large amount of the metal species although the Fe species were highly dispersed.

3.2. Syngas-to-Hydrocarbons Reaction. Since syngas produced from biomass contains generally lower hydrogen concentrations than syngas produced from CH_4 [4], it must be necessary to simultaneously generate hydrogen during the conversion of syngas to hydrocarbons in order to improve the producibility of hydrocarbons. The use of a hybrid catalyst composed of an FTS catalyst and a WGS catalyst will efficiently produce hydrocarbons from H_2 -deficient syngas as follows: (1) the CO hydrogenation to hydrocarbons over an FTS catalyst results in the generation of H_2O ; (2) generated H_2O reacts with CO over a WGS catalyst to generate hydrogen; and (3) generated hydrogen is used in the FTS:

3.2.1. Effect of Metal Species in WGS Catalyst on Catalytic Properties. We investigated the catalytic properties of a hybrid catalyst containing the metal-added Fe-based catalyst as a WGS catalyst in the conversion of H_2 -deficient syngas to hydrocarbons. Considering the use of syngas produced from biomass, syngas with the H_2/CO molar ratio of 1 was employed as a reactant gas in the present study. The metal-added Fe-based catalyst was centered together with 20 wt.% Co supported on beta zeolite (Co/ β) as an FTS catalyst in the reactor. Figure 7 shows the results of the conversion of H_2 -deficient syngas to hydrocarbons over Co/ β and the hybrid catalysts as a function of time on stream. Figure 7(a) clearly shows the improvement of the CO conversion by employing the Fe-based WGS catalyst together with the FTS catalyst through the reaction times. When Co/ β was used alone, the formation of CO_2 was not observed during the reaction (Figure 7(b)), indicating that CO was converted through only the FTS over Co/ β due to a low ability of Co species for the WGS reaction [38]. By contrast, the formation of CO_2 was observed when the hybrid catalysts containing the Fe-based WGS catalyst were used, regardless of the added metal species. Since no steam was introduced to the catalyst bed in the present study, CO_2 should be produced through the WGS reaction with H_2O generated in the CO hydrogenation over Co/ β , and hydrogen was simultaneously generated. Thus, it is indicated that the improvement of the CO conversion of the hybrid catalyst was derived from the WGS reaction. Moreover, it is also assumed that the hydrogenation concentration in the reaction system would be increased through the WGS reaction.

FIGURE 7: CO conversion (a) and the formation rate of CO₂ (b) in the conversion of syngas to hydrocarbons over hybrid catalysts containing FeCu and metal-added Fe-based catalysts. Reaction conditions: cat.: 1.5 g Co/ β , 1.95 g hybrid catalyst (1.5 g Co/ β and 0.45 g FeCu) and 2.0 g hybrid catalyst (1.5 g Co/ β and 0.5 g metal-added Fe-based catalyst); pressure: 1.0 MPa; W/F = 16.3 g_{cat}. h mol⁻¹; H₂/CO = 1.

As shown in Figure 7(b), the formation of CO₂ was also dependent on the Fe-based WGS catalysts; the space time yields (STY) of CO₂ at 0.5 h were in the order of FeCu > Mn-FeCu > Ce-FeCu > 10 wt.% Zr-FeCu > 20 wt.% Zr-FeCu. The formation rate of CO₂ of all the catalysts was gradually declined through the reaction. After 6.5 h of the reaction time, the hybrid catalyst with Mn-FeCu exhibited the highest CO₂ formation rate, and the other hybrid catalysts with the metal-added Fe-based catalyst showed similar CO₂ formation rates. These results indicate that Mn species in the Fe-based catalyst enhanced the catalytic activity for the WGS reaction and the catalyst durability in the CO hydrogenation, leading to an increase in the CO conversion, while Zr and Ce species hardly had positive effects for the WGS activity. In contrast, the CO conversion of Zr-FeCu was similar to that of Mn-FeCu, suggesting that Zr species improved the activity of the Fe-based catalyst for the FTS. However, increasing the amount of Zr from 10 wt.% to 20 wt.% decreased the CO conversion due to the decrease in the amount of the Fe species in the catalyst. The doping of metal species to Fe-based catalysts showed positive effects on catalytic performances for the CO hydrogenation and the WGS reaction [18–20, 34, 39, 40]. In the present study, the improvement of the catalytic activity would be derived from the high dispersion of the Fe species and the formation of active sites by the interaction of the Fe species with the Mn or Zr species. In the case of Ce-FeCu, the improvement of both activities for the CO hydrogenation and the WGS reaction was not observed due to low steam concentrations [41].

Table 2 summarizes the catalytic properties of the hybrid catalysts in the conversion of H₂-deficient syngas to hydrocarbons. The formation rate of hydrocarbons of the hybrid catalyst was increased by adding the metal species to FeCu in comparison with the hybrid catalyst containing FeCu. In the hydrocarbon distributions, the formation of C₅–C₁₁ hydrocarbons, which corresponds to gasoline fractions, was improved by using the hybrid catalysts, in particularly the hybrid catalysts containing Mn-FeCu or Ce-FeCu that exhibited high values of the C₅–C₁₁ hydrocarbon distribution. By contrast, the formation of hydrocarbons with carbon number more than 12 was suppressed when the Fe-based catalyst was employed together with Co/ β . Lohitharn et al. have reported that transition-metal-added Fe-based catalysts showed a similar hydrocarbon selectivity to that of an Fe-based catalyst without the addition of metal species [18, 19]. Thus, it is suggested that beta zeolite in the hybrid catalyst influenced the hydrocarbon distribution due to a high ability of the isomerization/cracking of hydrocarbons. Considering the generation of hydrogen through the WGS reaction over the Fe-based catalyst as shown in Figure 7(b), it is assumed that the increase in the hydrogen concentration would lead to the improvement of the spillover effect for the cracking of large hydrocarbons over acid sites or to the suppression of the carbon chain growth due to the hydrogenation of carbonaceous intermediates.

3.2.2. Stabilization of WGS Catalyst by Loading of Pd. The catalytic activity for the WGS reaction has been improved

TABLE 2: The results of the conversion of syngas to hydrocarbons over hybrid catalysts for reaction time of 6.5 h at 513 K^a.

	Without FeCu	FeCu ^b	Zr-FeCu (10 wt.% Zr)	Zr-FeCu (20 wt.% Zr)	Mn-FeCu	Ce-FeCu	Pd/Mn-FeCu
CO conv. (%)	35.2	41.7	45.1	40.0	45.0	39.5	44.8
CO ₂ STY (mol kg ⁻¹ h ⁻¹)	0	1.75	1.50	1.36	1.92	1.25	2.65
H.C. STY (mol kg ⁻¹ h ⁻¹)	2.48	2.16	2.38	2.30	2.61	2.54	2.35
H.C. distribution (C-%)							
CH ₄	31.8	36.7	33.8	34.3	33.2	31.4	36.6
C ₂ -C ₄	13.5	12.7	11.3	12.7	10.4	11.5	11.8
C ₅ -C ₁₁	38.5	43.9	41.1	36.7	45.9	48.2	41.9
C ₁₂ ⁺	16.1	6.7	13.7	16.3	10.5	8.9	9.7

^aReaction conditions: cat.: 2.0 g hybrid catalyst (1.5 g Co/ β and 0.5 g Fe-based catalyst); pressure: 1.0 MPa; W/F = 16.3 g_{cat.} h mol⁻¹; H₂/CO = 1.

^b1.95 g hybrid catalyst (1.5 g Co/ β and 0.45 g Fe-based catalyst).

FIGURE 8: CO conversion (a) and the formation rate of CO₂ (b) in the conversion of syngas to hydrocarbons over hybrid catalysts containing Mn-FeCu and Pd/Mn-FeCu. Reaction conditions: cat.: 2.0 g hybrid catalyst (1.5 g Co/ β and 0.5 g Fe-based catalyst); pressure, 1.0 MPa; W/F = 16.3 g_{cat.} h mol⁻¹; H₂/CO = 1.

by loading Pd on WGS catalysts due to the promotion of the redox properties of iron oxides [42]. In addition, an increase in the hydrogen concentration through the WGS reaction will lead to suppressing the deactivation [43]. In order to improve the activity and durability of the Fe-based WGS catalyst, 1 wt.% Pd species was loaded on 10 wt.% Mn-FeCu by impregnation with 4.6 wt.% Pd(NH₃)₂(NO₃)₂ aqueous solution. The catalytic properties of the hybrid catalyst composed of the Pd/Mn-FeCu with Co/ β were evaluated in the conversion of H₂-deficient syngas to hydrocarbons. The results are shown in Table 2 and Figure 8. Pd/Mn-FeCu exhibited a similar CO conversion to that of Mn-FeCu during the reaction. Meanwhile, the formation of CO₂ (H₂ generation) in

the WGS reaction was improved by loading Pd on Mn-FeCu. Furthermore, the gradual deactivation was observed on Mn-FeCu in the WGS reaction, while the CO₂ formation rate over Pd/Mn-FeCu was kept at ca. 2.6 mol kmol kg⁻¹ h⁻¹ even after 6.5 h of the reaction. In our previous findings, the deactivation derived from the deposition of carbonaceous species was suppressed by loading metal species with a high hydrogenation ability on ZSM-5, which was a part of a hybrid catalyst, in the syngas conversion to hydrocarbons via the methanol formation [44, 45]. Thus, Pd species on Mn-FeCu was supposed to readily activate hydrogen generated through the WGS reaction to decompose carbonaceous species, which were formed through the FTS, on active sites of the catalyst,

leading to the mitigation of the deactivation of the WGS catalyst.

In the hydrocarbon distribution, the loading of Pd species enhanced the formation of light hydrocarbons; in particular the selectivity to methane was increased to 36.6% in comparison with that of Mn-FeCu (Table 2). The high hydrogenation ability of Pd may lead to accelerate the hydrogenation of carbonaceous intermediates on active sites to form hydrocarbons with short chains prior to sufficient chain growth.

4. Conclusions

Metal-composite Fe-based catalysts with nanosized crystallites were synthesized by the addition of metal species such as Mn, Zr, and Ce into an Fe-based catalyst. The metal-added Fe-based catalysts exhibited much higher specific surface area than the conventional Fe-based catalyst due to the formation of mesoporous voids surrounded by the nanosized crystallites. The metal-added Fe-based catalyst as a WGS catalyst was mixed with Co/ β as an FTS catalyst to prepare a hybrid catalyst. The catalytic properties of the hybrid catalyst were investigated in the hydrocarbon production from syngas with the low H_2/CO ratio of 1, where hydrogen was deficient for the conversion of all CO to hydrocarbons. The use of the hybrid catalyst resulted in the formation of CO_2 , which corresponds to the simultaneous generation of hydrogen through the WGS reaction, regardless of the type of the added metal species, although no CO_2 was formed over Co/ β alone. Among the catalysts, the hybrid catalyst containing the Mn-added Fe-based catalyst exhibited the highest activity for the CO hydrogenation and the WGS reaction with the CO conversion of 45.0%, the STY of hydrocarbons of $2.61 \text{ mol kmol kg}^{-1} \text{ h}^{-1}$, and the STY of CO_2 of $1.92 \text{ mol kg}^{-1} \text{ h}^{-1}$ after 6.5 h of the reaction; furthermore, a high durability of the catalyst was observed during the reaction. Moreover, the loading of Pd species on the Mn-added Fe-based catalyst improved the durability due to the high hydrogenation ability of Pd species.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This work was supported by JSPS KAKENHI Grant no. 24560950.

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