Low Temperature Synthesis of Liquid Hydrocarbons from Syngas on Composite Catalysts of Pd-doped Cu-Cr-Zn Mixed Oxides and an H-ZSM-5 Zeolite

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Synthesis of liquid hydrocarbons from syngas was studied at relatively low temperatures, below 300°C, using bifunctional composite catalysts composed of low-temperature type methanol-synthesis catalysts of Pd-doped Cu-Cr-Zn mixed oxides and an H-ZSM-5 zeolite. As a source of Zn component of the methanol synthesis catalyst, freshly prepared $\text{Zn}(\text{OH})_2$ from $\text{Zn}(\text{NO}_3)_2$ was more suitable than a commercial ZnO powder for higher hydrocarbon yields. Oxidation and successive reduction (O-R) treatments of the composite catalysts were carried out at 400°C and in the range of from 400 to 800°C. When the reduction temperature of O-R treatment was 600°C, the performance of the composite catalysts was appreciably improved. Syngas ($\text{H}_2/\text{CO}=2$) was converted to hydrocarbons, dimethyl ether, and CO_2 with selectivities of 44.1, 1.4, and 54.5%, respectively, at 35.8% CO conversion at 290°C, 20 atm, and 6,000 hourly space velocity. The space-time conversion of CO to liquid hydrocarbons ($\text{C}_4\sim\text{C}_{11}$) and the corresponding selectivity were 9.5 mol/l·h and 61.4%, respectively. By lowering the H_2/CO ratio of syngas from 2 to 1, the liquid hydrocarbon selectivity increased to 68.4% whereas the space-time conversion of CO to liquid hydrocarbon decreased.

1. Introduction

Conventional Fischer-Tropsch reaction obeys Schulz-Flory carbon-number distributions of the products resulting in low gasoline selectivity. After the success in selective gasoline synthesis from methanol using ZSM-5 zeolite^{1)~4)}, Mobil's researchers applied this shape selective zeolite, combining it with methanol-synthesis catalysts (MSC) to direct synthesis of high octane-value gasoline from syngas.⁵⁾ Since this work, syngas to gasoline (STG) reaction using this kind of composite catalysts has been studied by many researchers.^{6)~13)} STG reaction *via* methanol is theoretically advantageous for its nontrivial poly-step mechanism¹⁴⁾ which enables overcoming thermodynamical conversion restrictions of methanol synthesis. However, at the present stage, product distribution is inferior to that of methanol conversion over ZSM-5 catalyst (MTG), and there is still much room for improvement. In our previous work¹²⁾, the effect of modifying $\text{ZnO-Cr}_2\text{O}_3$ industrial methanol-synthesis catalysts on the performance of the composite catalysts was investigated.

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Palladium-doping and O-R treatment were effective for increasing gasoline yields. However, the catalyst activity was low, requiring such high temperature as 381°C to obtain satisfactory yields of hydrocarbons. Therefore, in this study, low-temperature type Pd-doped Cu-Cr-Zn catalysts were adopted as MSC, and they were combined with highly active H-ZSM-5.^{11),12)} Using these catalysts, syngas conversion was examined under considerably mild reaction conditions around 300°C and 20 atm.

2. Experimental

2.1 Preparation of Low-temperature Type Methanol-synthesis Catalysts

Palladium-doped Cu-Cr-Zn methanol-synthesis catalysts were prepared using the method reported in the literature¹⁵⁾ with some modification. The precipitate of $\text{Cu}(\text{OH})_2$ from $\text{Cu}(\text{NO}_3)_2$ using $\text{NH}_3\text{aq.}$ as the precipitant at pH=7.9 was kneaded with Cr_2O_3 and the mixture was allowed to dry at 75°C for 4 h, before grinding. An aqueous solution of $\text{Pd}(\text{NO}_3)_2$ was mixed with ZnO powder, varying its amount, followed by calcination in air at 400°C for 4 min. For preparing Zn component

Table 1 Composition of Catalysts Used

Symbol	Catalyst Composition (atomic ratio)	Source of Zn
M-1	Cu : Cr : Zn = 2 : 1 : 2	ZnO powder
M-2	Cu : Cr : Zn : Pd = 2 : 1 : 2 : 0.012	"
M-3	Cu : Cr : Zn : Pd = 2 : 1 : 2 : 0.05	"
M-4	Cu : Cr : Zn : Pd = 2 : 1 : 2 : 0.1	"
M-5	Cu : Cr : Zn : Pd = 2 : 1 : 2 : 0.1	Zn(NO ₃) ₂

from Zn(NO₃)₂, Pd(NO₃)₂ and Zn(NO₃)₂ were coprecipitated using Na₂CO₃aq. as the precipitant at pH=6.5. All precipitation procedures were conducted using a Yamato Kagaku homogenizer. These Pd-Zn and Cu-Cr mixture were mixed, using a Yamato Kagaku kneading apparatus, and reduced in a mixed gas containing 1.7% CO, 3.3% H₂, and 95% N₂ flowing at a rate of 50 ml/min and heating at a rate of 1.4°C/min up to 350°C. Five kinds of catalysts thus prepared were designated M-1~M-5 and listed in **Table 1**.

2.2 Preparation of Composite Catalysts

The H-ZSM-5, prepared by the method described in our previous paper^{(11),(12)}, was mixed with a MSC in a porcelain mortar without kneading. The mixture consisted of the same weight of each component. The mixed powder was first tableted then crushed to 8~15 mesh pieces.

2.3 Catalyst Characterization

The temperature programmed reduction (TPR) for MSC was conducted using a TG-DTA apparatus, Shimadzu DTG-30. A 15 mg portion of the catalyst sample was placed in a sample pan. To avoid possible influence of dehydration and/or decomposition of the metal salts on the TPR profile, the sample was heated to 350°C in N₂ flow. After cooling to room temperature, the sample was heated at a constant rate (2°C/min) in a 5% H₂-

95% N₂ mixed gas flow. X-ray powder diffraction analysis with CuK α radiation was conducted using a Rigaku Geiger-Flex 2013 with a wide source for identification and measurement of crystallite sizes of the catalysts.

2.4 Reaction Method

Reaction of methanol and hydrocarbon syntheses from syngas were carried out, usually under 20 atm, using the same flow-reaction apparatus used in our previous work⁽¹²⁾. A 0.5 ml portion of the catalyst was packed in a stainless steel tubular reactor of 6 mm i. d.. The ratio of H₂/CO of the reaction gas was 2 or 1. The reaction conditions were: $P=20$ atm, $T=220\sim340^\circ\text{C}$, and $SV=6,000\text{ h}^{-1}$. All products were analyzed as gas by TCD- and FID-type gas chromatographs. Details of liquid-hydrocarbon range were analyzed by an OV-101-coated capillary column using a Shimadzu CR1-B type degital integrator equipped with an FID gaschromatograph.

3. Results and Discussion

3.1 Effects of Pd Loading and Source of Zn on the TPR Profile and XRD Pattern

The TPR profiles and their differential curves for each catalyst are shown in **Figs. 1** and **2**, respectively. The palladium nonloaded sample, M-1, showed a rapid reduction around 150°C, and a slow and steady reduction above 200°C. Palladium loaded samples (M-2,3, and 4) were reduced at temperatures lower than these on M-1, and their temperature profiles were monotonous. **Figure 2** shows the difference more clearly. Palladium lowered the reduction temperature; however, the temperature at the maximum reduction rate (θ_m) shifted to a higher temperature and the peak was

Fig. 1 TPR Profiles for Pd-doped Cu-Cr-Zn Catalysts

Fig. 2 Differential Curves of TPR Profiles shown in Fig. 1

Fig. 3 XRD Pattern for each Pd-doped Cu-Cr-Zn Catalyst after Reduction

broadened. On the other hand, catalyst M-5, in which Zn source and Pd-loading method were different from those of the others, showed a different temperature profile. The θ_m was the lowest (150 °C) and the maximum reduction rate (rm) was the largest ($\approx 7 \times 10^{-5}$ mg/mg·min). These observations must reflect that Pd was dispersed more finely and acted more effectively as a transport agency for hydrogen spillover. The degree of reduction was calculated for each MSC, based on the assumption that $\text{CuO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{ZnO} \cdot \text{PdO}$ was reduced to $\text{CuO}_x \cdot \text{Cr}_2\text{O}_3 \cdot \text{ZnO} \cdot \text{Pd}$ during the course of reduction. The results are as follows: $X=0.76$ (M-1), 0.46 (M-2), 0.55 (M-3), 0.27 (M-4), and 0.05 (M-5). The values of X for M-4 and M-5 are very low. In such cases, there is possibility that Cr_2O_3 and ZnO can be partly reduced by the action of Pd even in these lower temperature regions.

Figure 3 shows the XRD patterns of these catalysts. A set of patterns for M-1~M-4 catalysts

shows higher crystallinity than that of M-5. In every XRD pattern, the existence of metallic Cu can be observed. It is noted that the peak of Cu is low in M-2 and M-5.

3.2 Effects of Palladium Loading and Zn Source of MSC on Methanol Synthesis

The performance of methanol synthesis reaction for the five kinds of MSC was examined. The results are summarized in **Table 2**. The activity of each catalyst was expressed as space-time yield (STY: mol/l·h). In **Fig. 4**, the methanol STY was plotted against reaction temperature. When MSC was not doped with Pd (M-1), the maximum MeOH STY (3.4 mol/l·h) was observed at 292°C. As shown in **Fig. 4**, all Pd-doped MSC's (M-2~M-5) had higher activity than that of M-1. The temperature profiles of MeOH STY for Pd-doped MSC's were different from each other, and the maximum MeOH STY (4.9 mol/l·h) was obtained at 270°C by M-2 in which Pd loading was least.

Table 2 Performance of Pd-doped Cu-Cr-Zn Catalysts for Methanol Synthesis

Catalyst	Temp. Co (°C)	Conv. (%)	STY (mol/l·h)			Selectivity (C-mol%)					
			MeOH	MeOMe	CH ₄	MeOH	MeOMe	CH ₄	C ₂ ⁺	CO ₂	MeOH+MeOMe
M-1	251	4.8	2.3	0.4	0.2	46.4	16.9	4.5	3.6	28.6	63.3
	272	7.7	3.0	0.5	0.4	44.0	14.8	6.0	8.8	26.4	58.8
	292	9.3	3.4	0.6	0.6	39.4	13.1	6.8	13.9	26.8	52.5
M-2	248	6.3	4.1	0.8	0.1	63.7	24.9	1.0	0.3	10.1	88.6
	270	9.4	4.9	1.5	0.2	49.9	31.2	1.8	1.8	15.3	81.1
	291	10.2	3.4	1.9	0.4	32.7	36.2	3.3	5.2	22.6	68.9
M-3	246	5.4	3.4	0.7	0.1	62.6	26.1	1.4	1.1	8.8	88.7
	270	8.2	3.8	1.3	0.1	49.1	34.8	1.8	1.4	12.9	83.9
	298	11.1	3.6	2.1	0.4	32.9	39.2	3.4	4.2	20.3	72.1
M-4	240	4.9	2.7	0.6	0.1	59.3	25.0	1.2	0.3	14.2	84.3
	265	7.5	3.7	1.0	0.1	50.1	25.3	2.1	2.3	20.2	75.4
	290	9.6	3.5	1.4	0.4	35.6	28.3	3.7	6.0	26.4	63.9
M-5	253	7.2	4.3	0.3	0.2	68.4	10.1	3.4	3.9	14.2	78.5
	278	9.9	4.3	0.4	0.4	51.7	10.0	5.3	10.1	22.9	61.7
	295	10.3	3.9	0.6	0.7	38.7	12.0	6.4	15.9	27.0	50.7

Reaction conditions: H₂/CO=2, P=20 atm, SV=6,000 h⁻¹ Reaction conditions: H₂/CO=2, P=20 atm, SV=6,000 h⁻¹

Fig. 4 Temperature Dependence of MeOH STY for each Pd-doped Cu-Cr-Zn Catalyst

○●: Commercial ZnO powder was used
 △▲: Freshly prepared Zn(OH)₂ from Zn(NO₃)₂ was used. Reaction conditions: H₂/CO=2, P=20 atm, T=270±5°C, SV=6,000 h⁻¹

Fig. 5 Effect of the Amount of Pd on the MeOH STY and Cu(111) Peak Intensity of XRD

Moreover, CO₂ selectivity was considerably lower at that temperature. When, in stead of using ZnO powder (M-4), Zn and Pd components were simultaneously incorporated into Cu-Cr mixed oxides by coprecipitation (M-5), as described in the experimental section, MeOH STY increased especially at lower temperatures. The highly active catalysts M-2 and M-5 showed low oxidation states as mentioned above. Relative intensities of Cu(111) and MeOH STY were plotted against Pd/Cu atomic ratio (Fig. 5). Since the XRD peak of Cu₂O was masked by Cu peak¹⁶⁾, the Cu peak intensity was adopted as the index of Cu reduction state. Figure 5 shows inverse correlation between intensity and MeOH STY, and the maximum MeOH STY was obtained by low Pd loading; it also showed that when freshly prepared Zn(OH)₂ from Zn(NO₃)₂ was used as Zn source, the catalyst exhibited a better performance than when commercial ZnO was used.

3.3 Activity of Pd-doped Cu-Cr-Zn/H-ZSM-5 Composite Catalysts for Syngas Conversion

Each of the Pd-doped Cu-Cr-Zn catalysts (M-2~M-5) mixed with an equivalent weight of H-ZSM-5 was ground in a porcelain mortar to a fine powder which was tableted then crushed to 8~15 mesh pieces for use.

Hydrocarbon-synthesis activities of these composite catalysts are expressed as space-time conversion (STC_{HC} mol/l·h) of CO, and shown in Fig. 6. Carbon monoxide STC for hydrocarbon formation was calculated from all hydrocarbons produced. For a set of composite catalysts whose Zn component was derived from commercial ZnO powder (designated as MZ-1~MZ-4), the CO STC_{HC}

Reaction conditions: $H_2/CO=2$, $P=20$ atm, $SV=6,000$ h^{-1}

Fig. 6 Temperature Dependence of CO STC to Hydrocarbons for each Composite Catalyst

●: Commercial ZnO powder was used
○: Freshly prepared $Zn(OH)_2$ from $Zn(NO_3)_2$ was used
Reaction conditions: $H_2/CO=2$, $P=20$ atm, $T=270 \pm 5$ $^{\circ}C$, $SV=6,000$ h^{-1}

Fig. 7 Effect of the Amount of Pd on Hydrocarbon Distribution and CO STC/(MeOH STY + 2MeOMe STY)

decreased by Pd addition in the MSC and had a minimum at Pd/Cu concentration 0.006 (MZ-2). Although the effect of Pd on MSC catalysts M-2~M-5 was positive for methanol synthesis, it was negative for hydrocarbon synthesis when Pd was combined with H-ZSM-5. On the other hand, the composite catalyst whose Zn component was derived from $Zn(NO_3)_2$ (MZ-5) showed the highest CO STC_{HC} in spite of its high Pd content.

In Fig. 7, the effects of Pd content of MSC on the distribution of hydrocarbons produced and CO STC_{HC}/(MeOH STY + 2MeOMe STY) are shown,

where the space-time yields of MeOH and MeOMe were obtained on the methanol synthesis catalysts (M-1~M-5) in the absence of H-ZSM-5, and CO STC_{HC} was obtained on the composite catalysts (MZ-1~MZ-5). Therefore, the value of this ratio can be regarded as the index for estimating the nontrivial polystep mechanism proposed by Weisz¹⁴. As for hydrocarbon distribution, C₄⁺ hydrocarbons decreased and ethane and propane increased and aromatics were negligible for all catalysts by addition of a small amount of Pd (≈ 0.006 Pd/Cu, atomic ratio). As has already been pointed out by Fujimoto et al. that olefin-lean feature of the hydrocarbons produced in the syngas conversion on Cu-Zn-Al/H-ZSM-5⁸) and Pd/SiO₂/H-ZSM-5⁹) would be attributed to the hydrogenation by metal oxide or by metal components of the composite catalysts. It was proved that Pd brought about both methanol synthesis activity and olefin hydrogenation activity.

As shown in Fig. 7, CO STC_{HC}/(MeOH STY + 2MeOMe STY) had a minimum at Pd/Cu concentration = 0.006 (MZ-2), and this suggests that Pd inhibits hydrocarbon formation. This phenomenon can be considered as the suppression of autocatalytic conversion jump of MeOH¹⁷) on H-ZSM-5 because of the decrease in the concentration of surface olefinic precursors owing to hydrogenation caused by addition of Pd, especially in low concentrations.

3.4 Effect of O-R Treatment of Pd-doped Cu-Cr-Zn/H-ZSM-5 Composite Catalyst on Syngas Conversion

The results so far obtained have proved that excessive increase in the methanol-synthesis activity of MSC by Pd addition in the composite catalyst rather inhibits the carbon chain growth and lowers CO STC_{HC}.

It was previously reported that O-R treatment performed on a Pd-doped Zn-Cr MSC/H-ZSM-5 composite catalyst increased gasoline selectivity.¹²) Therefore, O-R treatment was first performed on MSC (M-5), then the treated M-5 was combined with H-ZSM-5 by mixing. The reduction temperature for O-R treatment was 600 $^{\circ}C$ (Exp. 2 in Table 3). Compared with the results of untreated catalyst Exp. 1, C₄⁺ selectivity increased by about 9% although CO conversion decreased by about 10%.

Next, the O-R treatment was performed on premixed catalysts of MSC (M-5) and H-ZSM-5 with the same conditions (Exp. 3). As a result, CO conversion further decreased by 5%, however, C₄⁺

Table 3 Effect of O-R Treatment on Syngas Conversion

Exp.	Catalyst	H ₂ Red. Temp. in O-R Treatment (°C)	CO Conv. (%)	CO STC (mol/l·h)			Hydrocarbon Distribution (C-mol%)									
				HC	MeOH	MeOMe	CO ₂	C ₁	C ₂	C ₃	C ₄	C ₂ -C ₄	C ₅ -C ₆	Aliph.	Arom.	C ₇ ⁺ total
1	M-5/H-ZSM-5a)	none	50.6	25.6	0.1	0.2	28.1	4.0	13.7	41.7	22.1	0	18.4	0.1		40.6
2	"	600b)	40.5	17.8	0	0	20.5	2.0	19.6	28.8	24.5	0	24.4	0.7		49.6
3	"	600c)	35.8	15.2	0.1	0.4	18.8	3.7	8.2	26.7	21.3	0	39.9	0.2		61.4
4	M-5/H-ZSM-5d)	none	20.7	9.2	0	0.8	8.6	6.6	13.1	35.8	20.8	0.2	23.5	0		44.3
5	"	400e)	69.4	27.1	0.5	1.2	28.7	9.5	10.4	40.8	19.4	0	19.9	0		39.3
6	"	500e)	42.2	18.5	0.7	2.8	18.7	9.6	9.6	31.0	16.7	0.2	32.9	0		49.6
7	"	600e)	28.2	11.4	0.1	0	11.6	8.4	8.8	23.4	19.2	0.4	39.7	0.1		59.0
8	"	700e)	14.9	5.8	0	0.1	5.3	12.0	16.7	22.7	18.1	0.6	29.9	0		48.0
9	"	800e)	10.1	4.4	0.1	0.1	3.8	16.9	18.7	24.3	15.5	1.4	23.2	0		38.7
10	M-1e)/H-ZSM-5d)	600e)	22.7	2.5	0.5	7.7	5.5	27.0	19.9	16.4	13.8	1.6	21.3	0		35.1

a) M-5 and H-ZSM-5 were mixed by powder blending method. b) The O-R treatment was conducted to M-5 before mixing with H-ZSM-5. c) The O-R treatment was conducted after mixing MSC with H-ZSM-5. d) MSC and H-ZSM-5 were mixed by powder-kneading method. e) Instead of ZnO powder of M-1, freshly prepared Zn(OH)₂ was used in the course of preparation.

selectivity increased up to 61.4%; the space-time conversion of CO to C₇⁺ (Exp. 3, 9.5 mol/(l·h)) was almost the same as that of the untreated catalyst (Exp. 1, 10.4 mol/(l·h)). These results suggest that a strong interaction between MSC and H-ZSM-5 has been brought about by O-R treatment.

To further investigate this interaction, MSC and H-ZSM-5 were mixed by kneading thoroughly in a mortar, and the effects of reduction temperature in the range from 400 to 800°C (Exp. 5~9) were investigated. By such kneading, CO conversion of untreated catalyst was lowered from 50.6% (Exp. 1) to 20.7% (Exp. 4). The CO conversion was maximum at the reduction temperature of 400°C (Exp. 5), and it was lower than that of the untreated catalyst above 700°C. Reduction at 600°C, C₇⁺ selectivity was maximum (59.0%). For comparison O-R treatment was conducted for non-Pd loaded Cu-Cr-Zn catalyst (Exp. 10), whose source of Zn component was Zn(NO₃)₂. Its CO STC_{HC} was very low, and the principal product was dimethyl ether. This suggests that the acidity of composite catalyst was lowered by redox-treatment more in the absence of Pd than in its presence. It seems reasonable to consider that, in the presence of Pd, the oxidation state of the mixed oxides, even that of ZnO, was reduced at such high temperature as 600°C by hydrogen spillover resulting in a lower basicity of the mixed oxides. On the other hand, when Pd was absent, the oxidation state of the mixed oxides, especially that of ZnO, was maintained at a higher level; thus the basicity of the mixed oxides, principally due to ZnO, would neutralize the acidity of the zeolite particle surface by thorough kneading.

In Fig. 8, X-ray diffraction patterns of these catalysts are shown. It is remarkable that peak intensities in the vicinity of 2θ=30, 35, 43, 50, and 63 degree increased and became sharp with increasing reduction temperature. In Fig. 9, the relations involving reduction temperature, the average crystallite size of MSC components, and the selectivity of C₇⁺ fraction are shown. This figure indicates that C₇⁺ selectivity increased with increasing CuCr₂O₄ crystallite size or with reduction temperature up to 600°C. However, above that temperature C₇⁺ selectivity decreased because the crystallite size of CuCr₂O₄ was reduced due probably to the separation of Cu phase.

Carbon number distributions of hydrocarbons produced by untreated and O-R treated (600°C) catalysts are plotted in Fig. 10. By O-R treatment,

Fig. 8 Effect of H_2 -reduction Temperature of O-R Treatment on the XRD Patterns of M-5/H-ZSM-5 Catalyst

Catalyst: M-5/H-ZSM-5
Reaction conditions: $H_2/CO=2$, $P=20$ atm, $T=290^\circ\text{C}$, $SV=6,000$ h^{-1}

Fig. 9 Effect of the Reduction Temperature of O-R Treatment on the Average Crystallite Size and C_4^+ Selectivity

C_2 and C_3 hydrocarbons decreased and the gasoline fraction increased. Furthermore, as can be seen in Exp. 5~9 of **Table 3**, the selectivity of lower olefins increased with increasing reduction temperature for the O-R treated.

This indicates that hydrogenation activity due to Pd and mixed oxides decreases because of sintering or recrystallization by O-R treatment. This trend is enhanced by lowering the H_2/CO ratio from 2 to 1; and as shown in **Table 3**, small amounts of

Catalyst: M-5/H-ZSM-5

Reaction conditions: $P=20$ atm, $T=290^\circ\text{C}$, $SV=6,000$ h^{-1}

Fig. 10 Effect of O-R Treatment and H_2/CO Ratio on Hydrocarbon Distribution

Additives: circle, none; triangle, 4.9% C_2H_4 ; square, 2.9% CO_2

Open symbol: Hydrocarbon, Filled symbol: MeOMe
Reaction conditions: $H_2/CO=2$, $P=20$ atm, $SV=6,000$ h^{-1}

Fig. 11 Effects of Additives on Syngas Conversion

lower olefins were produced by O-R treatment. Thus, suppression of lower-olefin hydrogenation is considered to be effective for increasing C_4^+ selectivity. The C_4^+ hydrocarbons were mostly branched.

3.5 Effect of Gaseous Additives on Syngas Conversion

Krier et al.¹⁸⁾ reported that a small amount of CO_2 remarkably accelerated the formation of methanol from syngas. It was also reported that lower olefins and several alcohols accelerated methanol conversion on H-ZSM-5 zeolite.^{17),19),20)} The au-

Table 4 Effect of Small Amount of Additives on the Products of Syngas Conversion

Syngas Composition (%)	CO 34.0 H ₂ 66.0	CO 29.2 H ₂ 67.9 CO ₂ 2.9	CO 30.6 H ₂ 64.5 C ₂ H ₄ 4.9
Additive (%)	—		
CO Conversion (%)	35.8	29.2	36.1
Hydrocarbon STY (mol/l·h)	4.5	2.9	14.5
C ₄ ⁺ STY (mol/l·h)	1.9	1.2	1.7
Carbon Selectivity in the Effluent Gas (C-mol%)			
Hydrocarbons	44.1	31.1	70.0
MeOMe+MeOH	1.4	2.7	0.2
CO ₂	54.5	66.2	29.8
Hydrocarbon Distribution in the Effluent Gas (C-mol%)			
C ₁	3.72	6.38	2.64
C ₂ (C ₂ ⁻)	8.22 (0)	8.69 (0)	62.86 (0)
C ₃ (C ₃ ⁻)	26.66 (0)	22.23 (0.30)	10.43 (0.05)
C ₄ (C ₄ ⁻)	21.34 (0)	18.48 (0)	9.19 (0)
C ₅	16.06	15.42	6.36
C ₆	17.52	17.56	6.26
C ₇	4.64	8.16	1.53
C ₈	0.88	1.87	0.40
C ₁₀ ⁺	0.78	0.60	0.23
A ₆	0	0	0
A ₇	0	0	0
A ₈	0.07	0.01	0.01
A ₉	0.05	0.02	0.02
A ₁₀	0.06	0.14	0.02
A ₁₁ ⁺	0	0.14	0
ΣC ₄ -C ₁₁	61.40	62.40	24.02

Catalyst : O-R (600°C H₂-red.) treated M-5/H-ZSM-5, see Table 3. Reaction conditions : P=20 atm, T=290°C, SV=6,000 h⁻¹

thors²¹⁾ found that the addition of a small concentration of C₄⁺ alcohols not only accelerated methanol conversion on H-ZSM-5, but also increased gasoline selectivity. It is of interest to apply these observations to syngas conversion on the composite catalyst to increase liquid hydrocarbon yields. Hence, syngas conversion was carried out by adding a small amount of C₂H₄ (4.9%) or CO₂ (2.9%). The results obtained at 290°C are listed in **Table 4**, and the space-time conversion of CO to hydrocarbons and dimethyl ether are plotted against reaction temperature in **Fig. 11**. In the case of CO₂ addition, only retardation in CO STC_{HC} occurred, and slight increases in C₇~C₈ paraffinic hydrocarbons and C₁₀⁺ aromatics were observed. In the case of C₂H₄ addition, C₂H₄ was hydrogenated completely to C₂H₆ even at 220°C. At such low temperature, CO conversion was below 5%; therefore CO STC_{HC}—expecting C₂H₆—was calculated. Moreover, enhancement in CO STC_{HC} was observed only below 280°C.

4. Conclusions

For syngas conversion to hydrocarbons on composite catalysts of Pd-doped Cu-Cr-Zn/H-ZSM-5 at low temperatures—below 300°C—the following conclusions were obtained.

(1) The space-time yield of MeOH of MSC (Cu-Cr-Zn) increased from 3.0 to 4.9 mol/l·h at

270°C by doping it with a small amount (0.4%) of Pd with maintained the proper reduction state of the catalyst during reaction.

(2) For hydrocarbon formation, the Zn component of the composite catalyst derived from freshly prepared Zn(OH)₂ was more effective than that derived from commercial ZnO powder.

(3) By O-R treatment performed at 600°C, C₃ hydrocarbon formation decreased, and the hydrocarbon distributions shifted to higher carbon numbers.

(4) The O-R treatment performed on the composite catalyst at 600°C enhanced its activity for production of liquid hydrocarbons (C₄~C₁₁). The space-time yield and selectivity of the liquid hydrocarbons were 9.5 mol/l·h and 61.4 C-mol%, respectively, under the following conditions: H₂/CO = 2, 20 atm, SV 6,000 h⁻¹, and 290°C.

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要 旨

パラジウムで修飾した銅-クロム-亜鉛複合酸化物ならびに H-ZSM-5 からなる複合触媒による合成ガスからの液状炭化水素の低温合成

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形状選択性ゼオライト ZSM-5 とメタノール合成触媒との複合触媒を用いて合成ガスから直接液状炭化水素を選択的に合成する反応は、通常三百数十 °C 以上の比較的高温と高圧の条件域で検討されてきた。しかし、このような温度域の場合、メタノール合成収量には限界があり、したがって液状炭化水素の収量もあまり高くできない。そこで本研究では、メタノール合成に有利な 300°C 以下の低温域で選択的に高収率で液状炭化水素を合成することを目的として、Pd で修飾した Cu-Cr-Zn 複合酸化物からなる低温型メタノール合成触媒と低温でもメタノール変換能をもつ高活性 H-ZSM-5 とを組合わせた触媒について、20 atm 下での流通法によって合成ガスの転化反応を検討した。

まず、メタノール合成触媒の TPR 挙動に対する触媒成分の影響を調べた。市販の ZnO に硝酸パラジウムを含浸させた場合は Pd の添加により還元開始温度は低くなったが、還元速度が最大となる温度はむしろ高く (200~220°C) になった。Zn(NO₃)₂ と Pd(NO₃)₂ の混合溶液から Na₂CO₃ で沈殿させて得た Zn(OH)₂-Pd(OH)₂ を用いた場合には、150°C の低温から急激に還元が起り、還元量も最大となった (Figs. 1,

2)。これらの触媒のメタノール合成活性は Pd 添加量が小さい場合 (Pd/Cu 原子比=0.006) に最大となった (Table 2, Fig. 4)。メタノール合成触媒と H-ZSM-5 との複合触媒による合成ガスからの炭化水素合成活性は、上記のようにして得た Zn(OH)₂-Pd(OH)₂ を用いたものが最も高かった (Fig. 6)。さらにこの触媒を酸化-還元すると生成物の選択率は変化し、400°C で酸化、600°C で水素還元した場合に、液状炭化水素の選択率は最大 (61.4%) となった (Table 3)。酸化-還元処理条件に対応して CuCr₂O₄ の粒子径が変化し、液状炭化水素の選択率とよく対応した (Fig. 9)。酸化-還元処理によりとくにプロパンが著しく減少して炭素数分布は高炭素数側 (C₅~C₉) に移動した。この傾向は H₂/CO 比を 2 から 1 に下げたときさらに明りょうに認められた (Fig. 10)。

原料の合成ガスに少量の CO₂ または C₂H₄ を添加したところ、どちらの場合も 280°C 以下でのジメチルエーテルの生成が大きく抑制された。CO₂ 添加の場合は単に反応抑制的な作用であったが、C₂H₄ 添加の場合は炭化水素生成に対する促進的効果が認められた (Fig. 11, Table 4)。

Keywords

Composite catalyst, Hydrocarbon synthesis, Mixed oxide, Palladium, Syngas conversion, Zeolite