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Co-Mn-Ru/Al_2O_3 catalyst for the production of high-calorific synthetic natural gas

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Abstract−Standard heating value for natural gas of South Korea, which imports LNG with high heating value is 10,400 kcal/Nm^3, while the heating value of conventional SNG is less than 9,500 kcal/Nm^3. Then the heating value of SNG should be enhanced to be used as city gas. In this study, Co-Mn-Ru/Al_2O_3 was applied in methanation to increase the heating value of the product gas. The role of each component and optimum composition where C_2-C_4 yield was highest were revealed. Mn enhanced the surface acidity, and promoted carbon-rich environment on the surface, which resulted in the increase of C_2-C_4 yield. Ru enhanced the reducibility of catalysts, and it resulted in high activity at lower temperature. As a result, optimum composition was 10Co-6Mn-2.5Ru/Al_2O_3. In addition, to replace Ru component, the reducibility of Co was enhanced by being reduced at higher temperature of 700 °C, and 20Co-Mn/Al_2O_3 catalysts achieved similar activity results to 10Co-6Mn-2.5Ru/Al_2O_3 without Ru.

Keywords: Methanation, Fischer-Tropsch, Cobalt Catalyst, Heating Value

INTRODUCTION

Petroleum is the main energy source for modern civilization, but is currently being depleted. Intensive efforts are ongoing to search for alternative energy sources. Among the various alternatives, coal is the most promising substitute for petroleum. The R/P value (reserve to production ratio) of coal is 113 years, while that of conventional oil and natural gas is 53.3 and 55.1 years, respectively [1]. Although shale gas and sand oil provide additional reserves for gas and oil, coal is the least expensive energy source available. However, coal emits large amounts of carbon dioxide per unit energy and ash during combustion. Thus, new technology for clean coal utilization and pollution reduction is required. Then, coal is converted to and used as natural gas via synthesis gas (syngas). The first step in the conversion of coal into synthetic gas is reforming, which is followed by methanation, the conversion of syngas into methane.

Ni/Al_2O_3 catalysts are typically used in methanation reactions; however, these Ni catalysts are highly selective for methane. Standard heating value for natural gas of South Korea and Japan who import liquefied natural gas (LNG) with high heating value is significantly high up to 11,000 kcal/Nm^3. Furthermore, remaining methane of shale gas after the separation of ethane may be used as gas fuel; then a process to enhance heating value is required. Heating value of methane is 9,523 kcal/Nm^3; then liquefied petroleum gas (LPG), which consists of propane and butane whose heating value is 24,179 and 32,059 kcal/Nm^3 each, is added to enhance the heating value of natural gas. However, as the price of oil increases, the price of LPG also increases, which dramatically increases the cost of adjusting the heating value of natural gas to a standard value.

To reduce LPG addition, the heating value of synthetic natural gas (SNG) can be enhanced by producing additional C_2-C_4 hydrocarbons during methanation, which have higher heating values per unit volume than methane. This "high calorific methanation," which enhances light paraffin selectivity to increase heating values, was first researched and named in Japan, whose standard heating value is also significantly high. The Inui group at Kyoto University and Kansai Coke & Chemical Company researched this reaction using a series of supported cobalt catalysts, and concluded that 10Co-6Mn-2Ru/Al_2O_3 displayed the best performance among tested catalysts [2,3]. However, catalytic properties that affect the product selectivity and other reaction characteristics are unknown.

In this study, the effect of each component in the Co-Mn-Ru/Al_2O_3 catalyst was examined by adjusting their respective amounts. After the role of each component revealed, the optimum composition of the catalyst was found by varying the weight fraction of each component.

EXPERIMENTAL

1. Catalyst Preparation

Catalysts were prepared by using the conventional incipient wetness impregnation method described in previous research [2]. A boehmite precursor (Disperal; Sasol) was converted into a mixed state of α and θ alumina phases by heating at 1,060 °C for 3 h.

Co/Al_2O_3 was obtained by impregnating $Co(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) dissolved in deionized water. After drying at 110 °C, Co/

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[‡] This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National Univerisity.

Al_2O_3 was calcined at 400 °C for 8 h. The mass fraction of cobalt was set at 5, 10, 20, and 30 wt%. Co-Mn/Al_2O_3 was obtained through the same procedure using $Mn(NO_3)_2\cdot 4H_2O$ (Sigma-Aldrich) as the manganese precursor. The mass fraction of cobalt was set at 10 and 20 wt%, and the manganese fraction was set at 0.2, 0.4, 0.6, and 0.8 times the cobalt amount.

To obtain Co-Mn-Ru/Al_2O_3, $RuCl_3\cdot H_2O$ (Aldrich) was used as the ruthenium precursor, which was dissolved in deionized water and loaded into the alumina support. After drying at 110 °C overnight, Ru/Al_2O_3 was heated at 350 °C for 3 h to remove chloride and convert ruthenium chloride into the oxide form. The cobalt and manganese precursors dissolved in deionized water were then impregnated on Ru/Al_2O_3. The mass fractions of cobalt and manganese were 10 wt% and 6 wt%, respectively, and the ruthenium fraction was set at 0.5, 1, 1.5, 2, and 2.5 wt%.

2. Activity Tests

Activity tests were performed in a continuous fixed bed reactor packed with 0.360 g of the catalyst. Each catalyst was reduced prior to the reaction under a flow of 10% hydrogen and balanced nitrogen for 1 h. Then, the feed gas, a mixture of hydrogen and carbon monoxide, was introduced into the reactor. The feed composition was fixed at CO : H_2=25 : 75 with a total volumetric flow of 30 mL/min. The reactor was then pressurized to 10 bar with the feed gas, and maintained at a constant pressure during the reaction. The feed and product gases were analyzed using a gas chromatograph (Younglin YL6500GC) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). A Carboxen 1000 column was connected to the TCD, and a Gas Pro column was connected to the FID. The conversion of carbon monoxide and selectivity for each product were calculated using Eqs. (1)-(3), and the yield of each product was calculated by multiplying the conversion and selectivity for each product.

Conversion of carbon monoxide (%)

$$=\left(1-\frac{\text{moles of CO remaining in product gas}}{\text{moles of CO in feed gas}}\right)\times 100 \tag{1}$$

Selectivity for hydrocarbons with carbon number of n (C_n) (%)

$$=\left(\frac{\text{n}\times\text{moles of Cn in product gas}}{\text{total moles of carbon in product gas}}\right)\times 100 \tag{2}$$

Selectivity for carbon dioxide (%)

$$=\left(\frac{\text{moles of carbon dioxide in product gas}}{\text{total moles of carbon in product gas}}\right)\times 100 \tag{3}$$

3. Characterization

Temperature programmed reduction (TPR) analysis was on a BELCAT-M-77 instrument (BEL Japan Inc.). A sample (0.05 g) was placed in a tubular quartz reactor, and was purged with helium (50 mL/min) for 1 h at 300 °C. H_2-TPR data were recorded while the temperature increased from 60 °C to 810 °C at 10 °C/min under a 30 mL/min flow of 5% H_2/N_2.

X-ray diffraction (XRD) patterns were obtained using a D/MAX-2500/PC diffractometer (Rigaku) operated at 40 kV and 100 mA with Cu Kα1 irradiation (λ=1.5406 Å), and data were collected in the range of 10° to 80° at a scanning rate of 4°/min. Si powder was used as the internal standard, and was added to the catalysts at one tenth of the total weight.

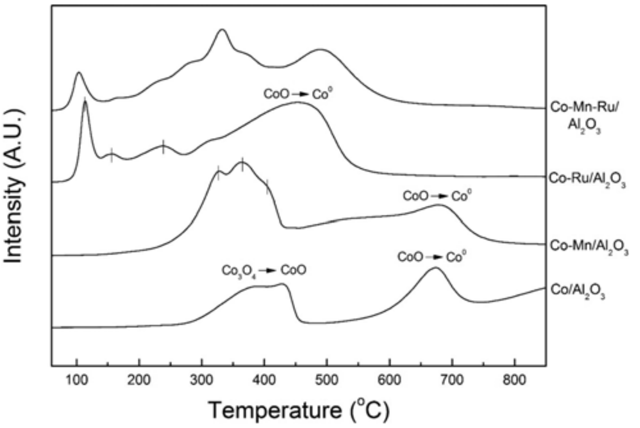

Fig. 1. H_2-TPR curves of cobalt catalyst: 10 wt% Co; 6 wt% Mn; and 2 wt% Ru.

RESULTS AND DISCUSSION

1. Role of Each Component in Co-Mn-Ru/Al_2O_3

1-1. H_2 Temperature Programmed Reduction

The H_2-TPR results of the Co/Al_2O_3 catalysts are displayed in Fig. 1. In the reduction curve of 10Co/Al_2O_3, dual peaks in the range of 300 °C to 450 °C indicate the reduction of Co_3O_4 to CoO, and the peak at 669 °C indicates the reduction of CoO to metallic Co. In the reduction curve of 10Co-6Mn/Al_2O_3, the peaks at 360 °C and 675 °C indicate the reductions of Co_3O_4 to CoO and CoO to metallic Co, respectively. The additional two peaks at 325 °C and 400 °C indicate the reductions of MnO_x to Mn_3O_4 and Mn_3O_4 to MnO, respectively [4]. Comparing the reduction curve of 10Co-6Mn/Al_2O_3 with that of Co/Al_2O_3, manganese addition shifted the reduction peak of Co_3O_4 to CoO to a slightly lower temperature (385-427 °C to 360 °C), while the reduction peak of CoO to metallic Co appeared at similar temperature (669 °C to 675 °C). This indicated that manganese promoted the reduction of Co_3O_4 to CoO. It was reported that the ease of the reduction of Co_3O_4 particle depends on the size of crystallites [5], and manganese addition increased the dispersion of Co particle [6]. It is also confirmed by the crystallite sizes in Table 1. The crystallite size of Co_3O_4 decreased from 31.0 nm to 22.5 nm by manganese addition; thus Co_3O_4 in Co-Mn/Al_2O_3 became easier to reduce compared to Co_3O_4 in Co/Al_2O_3; then the reduction peak of Co_3O_4 to CoO shifted to lower

Table 1. Crystallite sizes of the Co oxide crystallites[a]

Catalysts		Crystallite	2 Theta	Crystallite size[a] (nm)
Co/Al_2O_3	After calcination[b]	Co_3O_4	36.8°	31.0
	After reduction[c]	CoO	42.4°	17.3
Co-Mn/Al_2O_3	After calcination[b]	Co_3O_4	36.8°	22.5
	After reduction[c]	CoO	42.4°	15.7

[a] Calculated by applying Scherrer equation to the XRD peak at the given 2 theta position

[b] Calcined at 400 °C for 8 h

[c] Reduced at 400 °C for 1 h

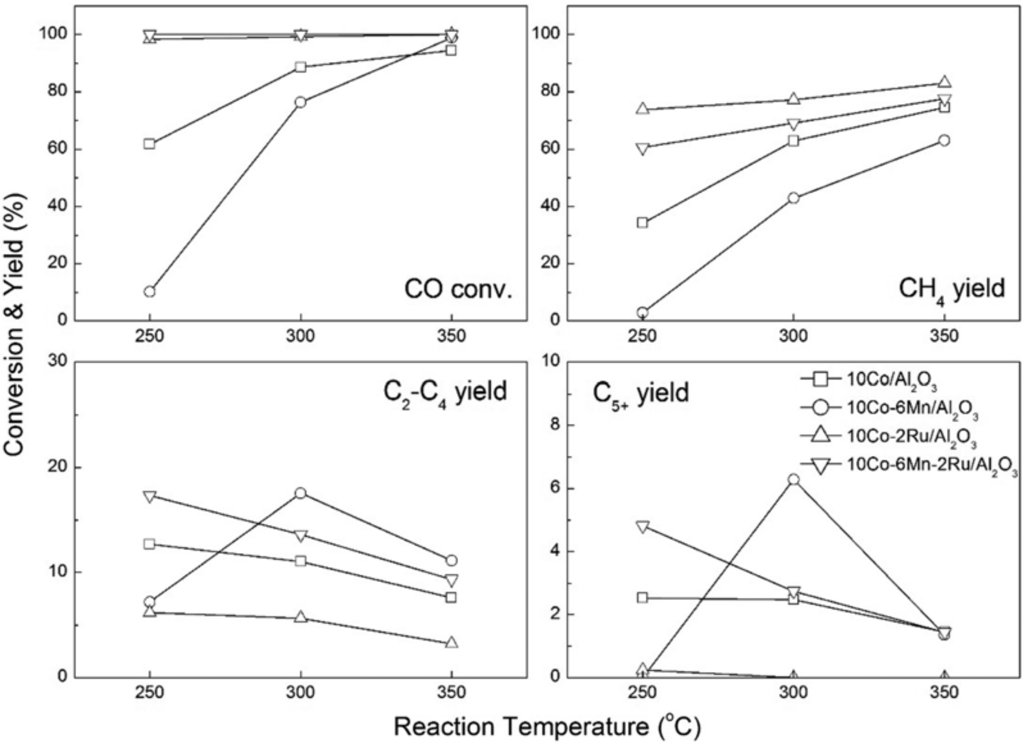

Fig. 2. Activity change upon addition Mn and Ru promoters to Co/Al_2O_3: reduced at 400 °C for 1 h under 50 mL/min of 10% H_2/N_2 prior to the reaction; feed gas composition CO : H_2=25 : 75; reaction pressure 10 bar; w/f=0.012 g/mL·min^{-1}.

temperature.

The peak shifts were more significant upon ruthenium addition. In the reduction curve of 10Co-2Ru/Al_2O_3, the peaks at 112 °C, 152 °C, 235 °C, and 455 °C indicate the reductions of Co_3O_4 near the ruthenium particle to CoO, RuO_2 to metallic Ru, remaining Co_3O_4 to CoO, and CoO to metallic Co [7]. Compared to the peaks of 10Co/Al_2O_3, Ru addition caused all peaks to shift to much lower temperatures. It is well known that Ru and noble metals gave hydrogen spillover ability, and "a small amount of noble metals can promote the reduction of cobalt alumina catalysts [8]." From TPR data, it was confirmed that the Co site in Co-Ru/Al_2O_3 began to be reduced to metallic Co under 400 °C, and the reducibility is higher at more-reduced Co site (Co^0>Co^{2+}>Co^{3+}). Thus it is clear that Ru greatly enhanced the reducibility of the Co site through H_2 spillover.

1-2. Change in Activity

Fig. 2 displays the activity change due to the incorporation of Mn and Ru into 10Co/Al_2O_3. Mn addition suppressed CO conversion, but increased C_{2+} hydrocarbons yield. TPR (Fig. 1) and XRD (Fig. 3) confirmed that added Mn existed as MnO, and this Mn^{2+} species acted as a Lewis acid, which interacted with the $O^{\delta-}$ of a CO molecule, increasing the dissociative adsorption of CO [9,10]. Without improvement in hydrogen adsorption, which may detach carbon species on the surface by converting to hydrocarbon, adsorbed carbon species remained on the catalyst surface, and this higher concentration of surface carbon species resulted in increased carbon chain growth and C_{2+} hydrocarbon yield. Thus, Mn addition enhanced the surface acidity, leading to higher C_2-C_4 hydrocarbon yields. However, activation of this sequence required higher temperatures, since the active site of Co was occupied by surface carbon species, resulting in the decrease in CO conversion and reaction rate.

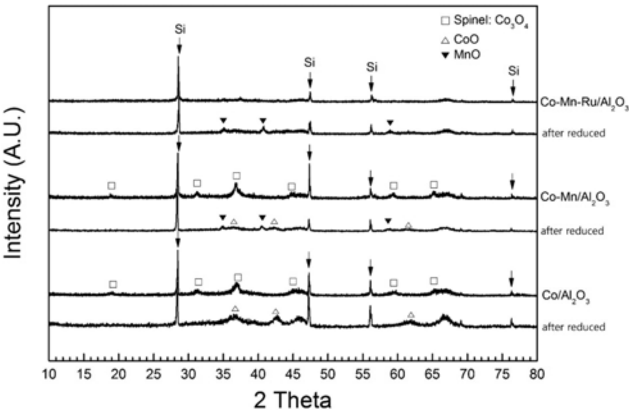

Fig. 3. XRD patterns of Co/Al_2O_3 catalysts before and after reduction with 10 wt% Si powder as the internal standard.

On the other hand, when Ru was added to Co/Al_2O_3, CO conversion reached nearly 100% even at temperatures as low as 250 °C. Ru addition enhanced the reducibility of the Co site, and metallic Co site, which was more electron-rich than Co oxides, interacted with $C^{\delta+}$ of a CO molecule; then CO conversion increased greatly. Ru also improved the dissociative adsorption of hydrogen molecules, and under this hydrogen-rich condition, surface carbon species was easily converted into methane and desorbed from the surface of the catalyst; then methane yield also increased greatly.

However, carbon chain growth was suppressed by the hydrogen-rich environment. Thus, Ru addition decreased C_{2+} hydrocarbon yield.

In conclusion, Mn addition enhanced carbon chain growth, while ruthenium improved conversion. Thus, Co-Mn-Ru/Al_2O_3 exhibited high CO conversion and C_2-C_4 hydrocarbon yield even at tem-

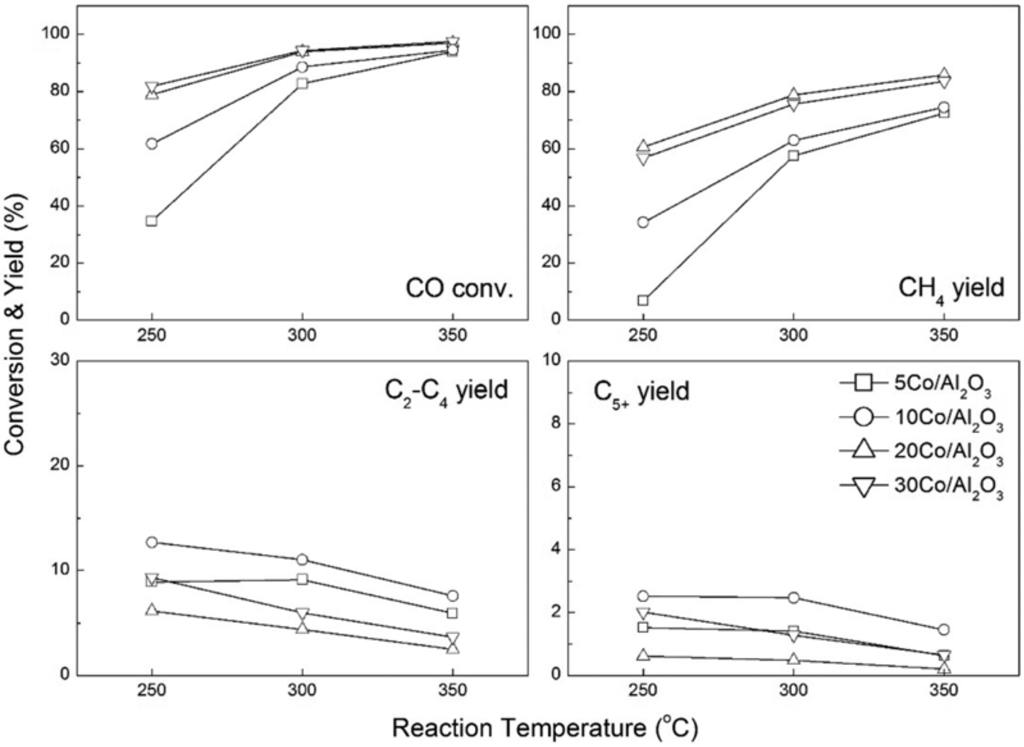

Fig. 4. Effect of Co amount in Co/Al_2O_3 on activity: reduced at 400 °C for 1 h under 50 mL/min of 10% H_2/N_2 prior to the reaction; feed gas composition CO : H_2=25 : 75; reaction pressure 10 bar; w/f=0.012 g/mL·min^{-1}.

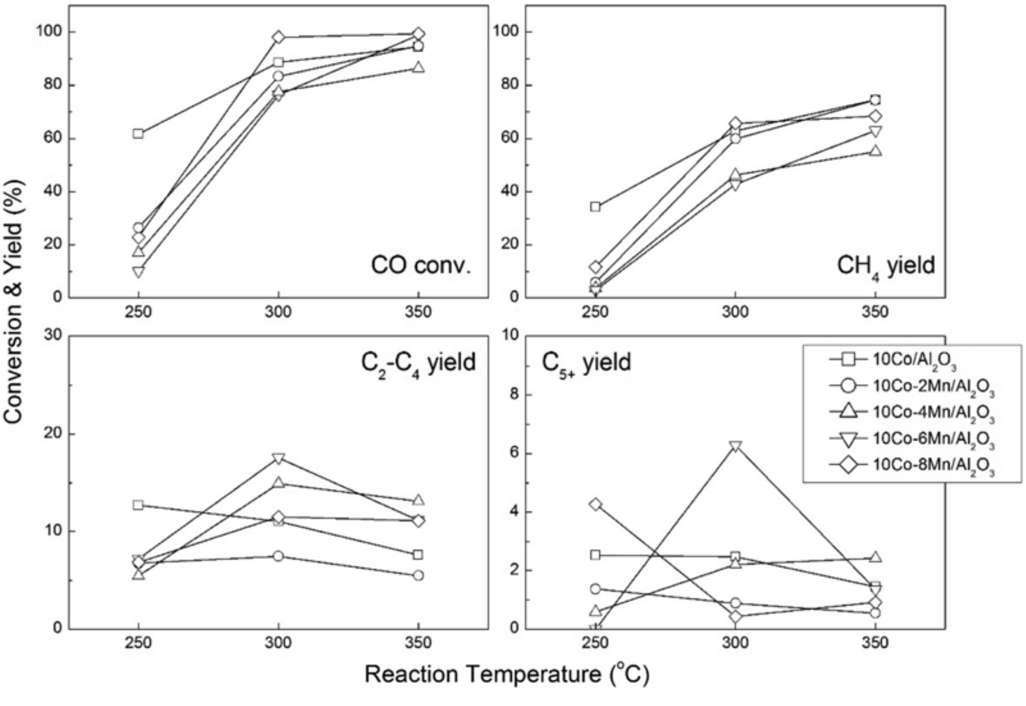

Fig. 5. Activity of 10Co-xMn/Al_2O_3 catalystsL: reduced at 400 °C for 1 h under 50 mL/min of 10% H_2/N_2 prior to the reaction; feed gas composition CO : H_2=25 : 75; reaction pressure 10 bar; w/f=0.012 g/mL·min^{-1}.

peratures as low as 250 °C. Carbon chain growth improved as temperature decreased because the surface carbon species is more easily desorbed at higher temperatures, and the increase in activity at low temperature resulted in higher C_{2+} hydrocarbon yield.

2. Optimizing Co-Mn-Ru/Al_2O_3

2-1. Optimum Fraction of Co-Mn-Ru/Al_2O_3

Fig. 4 displays the activity change of Co/Al_2O_3 as the amount of cobalt increases from 5 to 30 wt%. CO conversion initially increased as the amount of Co increased, but became nearly constant at over 20 wt%. It implied that the surface of the catalyst was saturated by Co over 20 wt%, and CO conversion depended on the number of active sites. On the other hand, C_{2+} hydrocarbon yield was highest using 10Co/Al_2O_3. This strongly indicates that the structure of the catalyst has a greater effect on carbon chain growth than the number of Co active sites [11].

Fig. 5 shows the activity change of 10Co-Mn/Al_2O_3 as the amount of Mn increases from 2 to 8 wt%. Upon Mn addition, activity at a low temperature of 250 °C decreased greatly, but CO conversion was restored above 300 °C. Mn addition enhanced carbon chain growth and C_{2+} hydrocarbon yield by acting as Lewis acid site, as mentioned above, but the relationship between activity change and Mn amount was unclear. Among tested catalysts, 10Co-6Mn/Al_2O_3 showed the highest C_{2+} hydrocarbon yield.

Fig. 6 gives the activity change of 10Co-6Mn-Ru/Al_2O_3 as the amount of Ru increases from 0.5 to 2.5 wt%. The promoting effect of ruthenium is clearly observed at only 0.5 wt%; great increase of CO conversion. All Ru-promoted catalysts achieved 100% CO conversion even at 250 °C. Furthermore, C_{2+} hydrocarbon yield increased greatly at 250 °C. As mentioned above, carbon chain growth is suppressed as the temperature is increased because the surface carbon species is easier to desorb at higher temperatures, which results in the increase of methane yield. Thus carbon chain growth probability was highest at 250 °C, and CO conversion at 250 °C increased greatly by adding Ru; then Co-Mn-Ru/Al_2O_3 catalysts showed high C_2-C_4 hydrocarbon yield over 15% at 250 °C. Among tested catalysts, 10Co-6Mn-2.5Ru/Al_2O_3 showed the highest C_2-C_4 hydrocarbon yield of up to 22.7% at 250 °C.

3. Replacing Ruthenium Fraction in the Catalyst

To save material cost for the synthesis of catalysts, Ru, which is one of the noble metals, should be reduced or substituted. Ru enhanced the reducibility of the Co site by reducing into metallic Co; then Ru could be replaced by increasing the reducibility of Co site by reducing catalysts at 700 °C where Co site reduced to metallic state, and the amount of Co site increased to enhance this higher temperature reduction effect further.

Fig. 7 displays the activity of 20Co-Mn/Al_2O_3 catalysts reduced at 700 °C for 1 h. Catalysts showed similar reactivity to 10Co-6Mn-2.5Ru/Al_2O_3 reduced at 400 °C for 1 h. 20Co-Mn/Al_2O_3 catalysts achieved 100% CO conversion at 250 °C without Ru addition. Only 20Co-16Mn/Al_2O_3 did not achieve 100% CO conversion at 250 °C, but achieved at 300 °C, and showed much higher C_2-C_4 hydrocarbon yield. C_2-C_4 hydrocarbon yield increased as the amount of Mn increased, and it might result from increasing the surface acidity due to MnO. As a result, CO conversion was enhanced by higher reducibility and larger amount of Co site, and C_2-C_4 hydrocarbon yield was also enhanced by promoting Mn.

4. Heating Value of the Product Gas

The heating value per unit volume of the product gas of 10Co-6Mn-2.5Ru/Al_2O_3 was calculated from the volumetric hydrocarbon fractions by summing the products of the volume fractions and heating values of pure gases in the C_1-C_5 range. Retained hydrogen, carbon monoxide, and carbon dioxide were excluded from

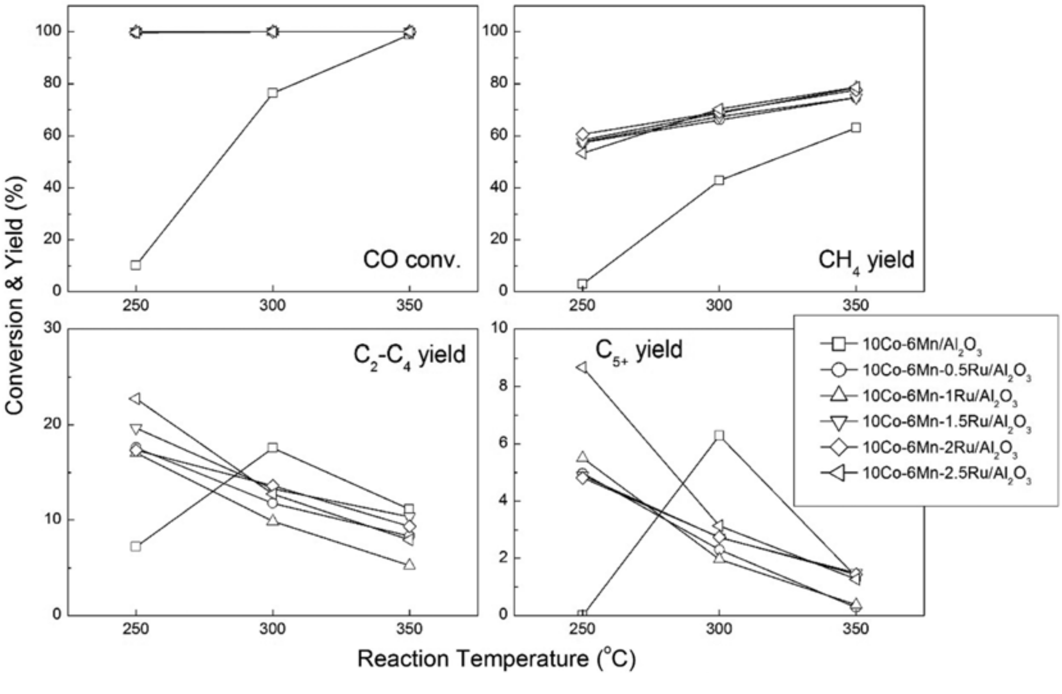

Fig. 6. Activity of 10Co-6Mn-xRu/Al_2O_3 catalysts: reduced at 400 °C for 1 h under 50 mL/min of 10% H_2/N_2 prior to the reaction; feed gas composition CO : H_2=25 : 75; reaction pressure 10 bar; w/f=0.012 g/mL·min^{-1}.

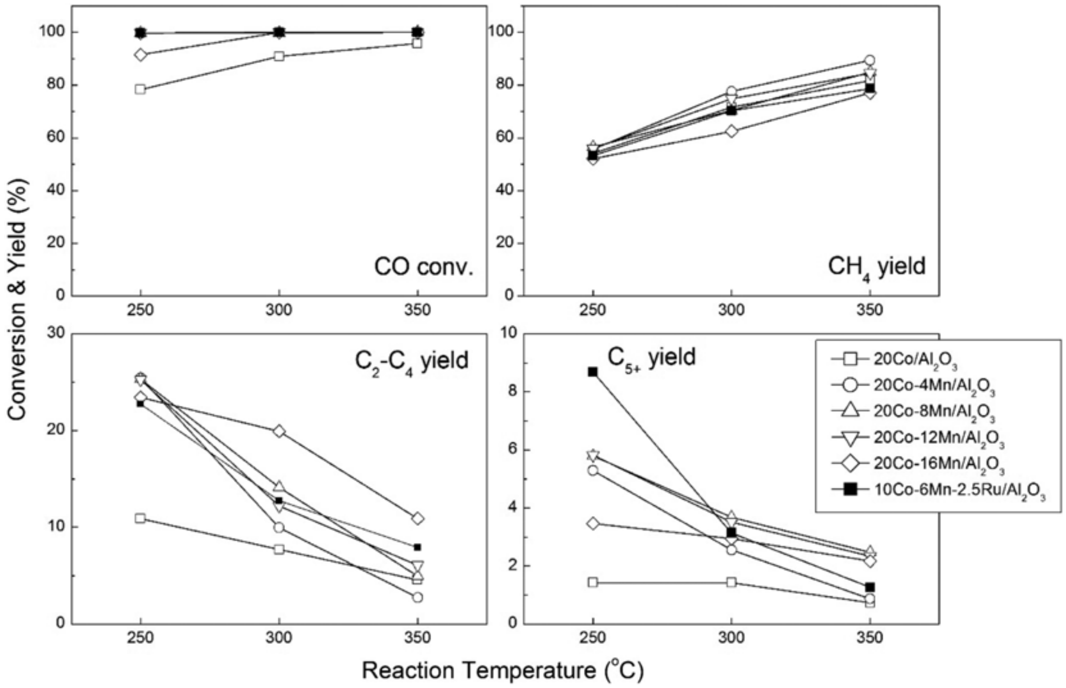

Fig. 7. Activity results of 20Co-xMn/Al_2O_3 catalysts: reduced at 700 °C for 1 hour under 50 mL/min of 10% H_2/N_2 before the reaction; feed gas composition CO : H_2=25 : 75; reaction pressure 10 bar; w/f=0.012 g/mL·min^{-1}.

Table 2. Calculated heating value of the product gas based on volumetric fraction of hydrocarbons

	Catalyst	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	n-C_5H_{12}	Calculated heating value (kcal/Nm^3)
Volume fraction (%)	10Co-6Mn-2.5Ru/Al_2O_3	86.0	5.5	4.5	2.6	1.4	11,623
	20Co-16Mn/ Al_2O_3	84.9	7.2	5.4	1.9	0.6	11,465
Heating value of pure gas (kcal/Nm^3)		9,523	16,814	24,179	32,059	41,077	

Reaction condition: Temperature 250 °C; pressure 10 bar; feed gas composition H_2/CO=3; w/f=0.012 g/mL·min^{-1}

the calculation. Table 2 shows the volume fractions of hydrocarbons, heating values of pure gases, and the calculated heating value of the product gas. The calculated heating value of the product gas of 10Co-6Mn-2.5Ru/Al_2O_3 and 20Co-16Mn/Al_2O_3 at 250 °C was 11,623 kcal/Nm^3 and 11,465 kcal/Nm^3, which is sufficient to replace LPG in enhancing the heating value of natural gas.

CONCLUSIONS

The Co-Mn-Ru/Al_2O_3 catalyst showed great activity in high-calorific methanation reactions. The Mn promoter existed as MnO after reduction at 400 °C under 10% H_2/N_2 gas. This MnO acted as a Lewis acid, which enhanced the surface acidity and increased carbon chain growth. On the other hand, Ru provided the catalyst with hydrogen spillover ability, enhancing both the reducibility of the Co site and the dissociative adsorption of hydrogen, and increasing CO conversion at lower temperatures. As a result, Co-Mn-Ru/Al_2O_3 showed high CO conversion and C_2-C_4 hydrocarbon yield even at temperatures as low as 250 °C.

After the role of each component was revealed, the optimum composition of Co-Mn-Ru/Al_2O_3 was studied: 10Co-6Mn-2.5Ru/Al_2O_3 showed the highest C_2-C_4 hydrocarbon yield among tested catalysts. To exclude Ru in the catalyst, the amount of Co site increased, and 20Co-Mn/Al_2O_3 catalysts were reduced at higher temperature of 700 °C. Due to enhanced reducibility and amount of Co site, 20Co-Mn/Al_2O_3 achieved 100% CO conversion at low temperature without Ru, and C_2-C_4 yield was also enhanced by Mn promotion. As a result, the calculated heating value of the product gas of 10Co-6Mn-2.5Ru/Al_2O_3 and 20Co-16Mn/Al_2O_3 at 250 °C were 11,623 kcal/Nm^3 and 11,465 kcal/Nm^3 each.

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