[Letter]

Additive Effect of Mn on Catalytic Activity of Ru/Al$_2$O$_3$ for Fischer–Tropsch Synthesis

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Ru/Al$_2$O$_3$ catalyst was investigated by using Mn addition for Fischer–Tropsch synthesis under pressurized conditions. On the basis of catalyst activity, selectivity and deactivation, small amount of Mn addition such as Mn/Al=1/19 molar ratio on Ru/Mn/Al$_2$O$_3$ was effective for improving the catalytic performance, where Ru/Al$_2$O$_3$ was deactivated in the slurry phase reaction. Under high pressure of 6 MPa, equilibrium CO conversion was estimated to be about 96%.

Keywords: Manganese addition, Ruthenium catalyst, Fischer–Tropsch synthesis, High pressure reaction

Fischer–Tropsch (FT) synthesis is the heart of the process for the production of middle distillate as well as clean diesel fuel from natural gas, coal or biomass derived synthesis gas (a mixture of CO and H$_2$)[1]. It is well known that Ru, Co and Fe can be utilized for FT synthesis in any way[2]~[4]. However, Ru metal from RuCl$_3$.nH$_2$O can be more effective to improve middle distillate yields and higher wax formation, which can be cracked into middle distillates at a same time by using suitable supports in the catalysts. The problem in the slurry phase FT reactor, which can be inhibited the hot spot formation, is catalyst deactivation[5]. Therefore, we need catalyst development with high activity and stability. In this view Mn as additive can be promoted FT catalyst. The addition of Mn strongly depends on the supports and the preparation methods to achieve better stability, activity and selectivity toward carbon chain growth probability[6],[7]. Previous report suggested that γ-Al$_2$O$_3$ support is more effective in the presence of Mn for FT synthesis[7]. In this letter, we investigated the additive effect of Mn to Al$_2$O$_3$ on catalyst performance for FT synthesis at low reaction temperature. We focus on the catalyst activity and stability by a small amount of Mn addition under pressurized conditions.

Ru catalysts were prepared by the impregnation method from γ-Al$_2$O$_3$ (Soekawa Chemicals, Japan) and MnO (Strem Chemicals, USA) with aqueous solution of RuCl$_3$.nH$_2$O (Soekawa Chemicals, Japan) and Mn(NO$_3$)$_2$.6H$_2$O (Wako Pure Chemical Industries, Ltd., Japan); and maintained the drying and calcination temperature[7]. These prepared catalysts are denoted as Ru/Al$_2$O$_3$, Ru/Mn/Al$_2$O$_3$ and Ru/MnO. The loading amount of Ru was 5 wt% and the molar ratio of Mn to Al was maintained in this study as 1/1 to 1/19. BET surface area of these catalysts is listed in Table 1.

FT synthesis was carried out in a 0.3 L autoclave slurry reactor under pressurized conditions. The catalyst was reduced by hydrogen at 473 K, 2 MPa for 5 h. After the pretreatment, catalyst was suspended by using 80 g hexadecane as a solvent under atmospheric pressure and room temperature. The amount of catalyst was 2.5 g and the partial pressure ratio of reactants was H$_2$/CO/Ar=6/3/1. The reactions were carried out at T= 493 K, P= 1–6 MPa, GHSV =1800 h^{-1}. The effluent gas and liquid hydrocarbons were analyzed with Shimadzu gas chromatographs in both FID and TCD detectors. The methods on XRD and XPS were described in our previous report[7]. Characterization results are also listed in Table 1.

Table 1 Properties of BET and XPS on Ru/Mn/Al$_2$O$_3$

Mn/Al ratio	BET (m^2/g)	Surface atomic concentrations in XPS (%)[a]					Atomic ratio, Cl/Mn
		Ru	Mn	Cl	O	Al	
0/100	81.3	1.3	–	0.9	60.0	37.8	–
1/19	80.2	2.3	0.3	0.7	60.0	36.7	2.3
1/4	69.4	3.2	2.5	2.2	59.3	32.8	0.9

[a] H$_2$ reduction at 473 K for 3 h inside the XPS chamber.

Table 2 represents the effect of Mn loading to Ru/Mn/Al$_2$O$_3$ for FT synthesis at 493 K and 2 MPa. Without Mn containing Ru/Al$_2$O$_3$ showed low CO conversion, and deactivation rate was clearly observed. On the other hand, the addition of small amounts of Mn to Ru/Mn/Al$_2$O$_3$ enhanced the catalytic activity remarkably. When Mn/Al ratio was used as 1/19, Ru/Mn/Al$_2$O$_3$ showed higher CO conversion than Ru/Al$_2$O$_3$, and the deactivation rate and methane selectivity were negligible with time on stream. In this condition, C$_5^+$ selectivity, olefin–paraffin ratio and carbon chain growth probability were about 94%, 0.73 and 0.92, respectively, and space time yield was about 0.26 mol/gh. On the other hand when Mn loading increased from 1/19 to 1/1 over Ru/Mn/Al$_2$O$_3$, CO conversion and C$_{10}^+$ selectivity decreased and, methane selectivity and deactivation rate increased significantly. From comparison over Ru/MnO and Ru/Mn/Al$_2$O$_3$, Ru/MnO showed much low CO conversion than Ru/Mn/Al$_2$O$_3$, and CO conversion was

"Fischer–Tropsch 合成のための Ru/Al$_2$O$_3$ 触媒への Mn の添加効果"

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about 3.6%. These results indicate that small amounts of Mn addition can play an important role for FT synthesis.

Figure 1 shows the reaction time dependence on CO conversion over Ru/Mn/Al$_2$O$_3$ catalyst for FT synthesis under pressurized conditions. In this experiment, Mn–Al ratio was used as 1/19 and reaction temperature was 493 K. CO conversion increased with increasing the pressure, and the conversion was very stable under pressurized conditions of 2, 4 and 6 MPa. In particular, high catalytic activity and high resistance to catalyst deactivation with time on stream were observed under pressure of 6 MPa, and equilibrium CO conversion was about 96%.

Table 2 Effect of Mn Loading to Ru/Mn/Al$_2$O$_3$ Catalyst for FT Synthesis

Mn/Al ratio	CO conv. (%)	Selectivity[a] (%)					STY[b] (mol /gh)	O/P[c]	D[d] (%)	α[e]
		C$_1$	C$_2$-C$_4$	C$_5$-C$_9$	C$_{10}$-C$_{20}$	C$_{21}^+$				
0/100	76.7	1.8	2.9	17.1	39.3	37.9	0.212	1.00	14.8	0.92
1/19	84.9	2.0	1.4	17.9	43.0	32.9	0.258	0.73	2.7	0.92
1/9	83.6	2.6	2.2	19.4	41.6	32.0	0.247	0.70	2.8	0.92
1/4	82.6	3.0	6.5	20.6	41.0	27.6	0.222	0.67	3.6	0.90
1/2	25.3	22.7	16.8	21.1	26.6	12.5	0.050	0.59	61.7	0.86
1/1	24.8	23.3	18.5	22.0	25.1	10.9	0.042	0.56	71.3	0.85
100/0	3.6	100	-	-	-	-	-	-	-	-

Reaction conditions: catalyst weight=2.5 g, H$_2$/CO =2, GHSV=1800 h^{-1}, T=493 K, P=2 MPa, TOS=39 h, H$_2$ reduction= 473 K.
Ru content was 5 wt%.
[a] Carbon-based selectivity.
[b] Space time yield on CO conversion and C$_5^+$ selectivity.
[c] Olefin/Paraffin ratio in C$_2$-C$_4$ hydrocarbon products.
[d] Deactivation rate: (CO conv. at 3 h - CO conv. at 39 h) / CO conv. at 3 h × 100.
[e] Carbon chain growth probability.

Figure 2 shows the XRD patterns of Ru/Al$_2$O$_3$, Ru/Mn/Al$_2$O$_3$ and Mn/Al$_2$O$_3$ with the various amounts of Mn loading. After catalyst calcination, the diffraction peaks assigned to the Mn$_2$O$_3$[8] were clearly observed over Mn/Al$_2$O$_3$ (Mn/Al=1/4) and Ru/Mn/Al$_2$O$_3$ (Mn/Al=1/2 and 1/1). The important point is that Mn$_2$O$_3$ was not observed over Ru/Mn/Al$_2$O$_3$ in between 1/19 and 1/4 Mn/Al ratio, while RuO$_2$[9] peaks with low intensity were observed over Ru/Mn/Al$_2$O$_3$. On the other hand, BET surface area and XPS results are presented in **Table 1**, and it is found that surface area decreased and Ru concentration increased with Mn loading over the catalyst and Cl was present on the catalyst surface. The ratio of Al/O in the concentration of oxygen and Al was observed as well according to the condition of Al$_2$O$_3$ compounds. Furthermore, at Mn/Al=1/19, Cl to Mn ratio was 2.3, and it is difficult to determine the Mn species by XPS measurement. More investigation is underway in the electronic state, which will be reported in the future study. Thus, it can be concluded that Ru/Mn/Al$_2$O$_3$ catalyst with Mn/Al=1/19 shows high FT activity and stability, in particular, under elevated pressure.
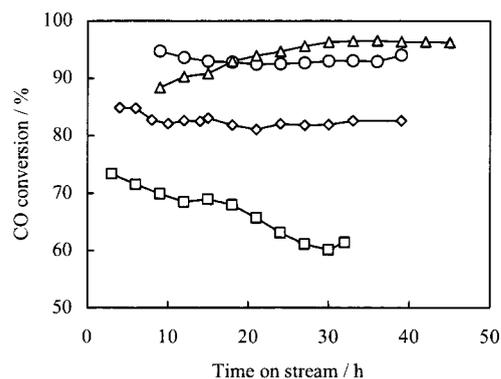

Fig. 1 Reaction Time Dependence of CO Conversion over Ru/Mn/Al$_2$O$_3$ Catalyst for FT Synthesis under Pressurized Conditions
(□) 1 MPa, (◊) 2 MPa, (o) 4 MPa, (△) 6 MPa. Ru content was 5 wt% and Mn to Al ratio was 1/19. Reaction conditions: catalyst weight=2.5 g, T=493 K, H$_2$/CO=2, GHSV=1800 h^{-1}, H$_2$ reduction=473 K.
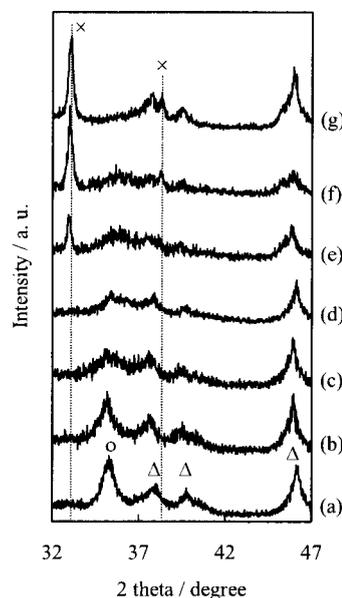

Fig. 2 XRD Patterns of (a) Ru/Al$_2$O$_3$, (b-f) Ru/Mn/Al$_2$O$_3$ and (g) Mn/Al$_2$O$_3$ after the Catalyst Calcination Treatment
Mn/Al ratio as (a) 0/100, (b) 1/19, (c) 1/9, (d) 1/4, (e) 1/2, (f) 1/1 and (g) 1/4. (o) RuO$_2$, (△) γ-Al$_2$O$_3$, (×) Mn$_2$O$_3$.

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