[Regular Paper]

Effects of Cr Addition on the Catalytic Properties of Ultrafine Particles of Co for Liquid Phase Fischer-Tropsch Synthesis

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The activities of Co-based ultrafine particles (UFP) catalysts for slurry phase Fischer-Tropsch (FT) synthesis were investigated at 270°C and 30 atm. Among the catalysts tested, Co-Cr UFP catalyst exhibited the highest activity. The activity and the selectivity of Co-Cr UFP catalyst for liquid-hydrocarbon production increased with increasing content of Cr, and it attained a maximum at about 2 wt%. Co-Cr supported on SiO₂ exhibited similar catalytic performances as those of Co-Cr UFP. There was a good relationship between catalytic activity and chemisorptive uptake of CO. Reducibility of Co was improved in the presence of Cr. Thus, we deduce that there was a maximum number of active sites due to the promoting effects of Cr on reduction of Co and on sintering of Co. Product distribution was found to be affected only by the size of Co particles.

1. Introduction

The surface properties of metals are dependent on the size of particles. The surface area increases with decreasing particle size, and extremely small particles exhibit different physical and chemical properties from those of large particles. Particles in the range from 10 to 1000 Å are usually called ultrafine particles and they have aroused much interest in their catalytic application.

Fischer-Tropsch (FT) synthesis is accompanied by extremely large heat evolution. To improve the characteristics of heat transfer, slurry phase synthesis has been developed¹⁾. However, one of the most serious drawbacks of the slurry phase FT synthesis is diffusional limitation for the reactants in the catalyst pores. One of the ways to overcome this disadvantage is to use extremely small catalyst particles which have nonporous structure and large surface areas. We have studied the application of ultrafine particles (UFP) as a catalyst for enhancing gas-/liquid-solid interface contact in a slurry reactor²⁻⁵⁾, and it has been found that Fe and Co UFP catalysts are more active and selective for production of liquid hydrocarbons than ordinary precipitated Fe and Co catalysts. A good catalytic performance was attained by proper physical and chemical pretreatments. The preoxidation of the

surface of Fe UFP suppressed sintering of UFP during the reaction, resulting in high catalytic activity⁶⁾. Our previous works have shown that the catalytic activity of Fe UFP for the slurry phase FT synthesis is significantly enhanced by modification with K⁷⁾ and Cu^{8),9)}. We have also reported¹⁰⁾ that Fe-MnO UFP catalyst exhibits high selectivity for olefin production. Colley and co-workers^{11),12)} have reported that selectivity of co-precipitated Co-MnO catalyst for production of liquid hydrocarbons was enhanced by addition of K and Cr.

The objective of our present study is to describe the effects of various additives on the catalytic performance of Co UFP for slurry phase FT synthesis. The UFP catalysts were prepared by the method of chemical deposition in the liquid phase.

2. Experimental

2.1. Apparatus and Procedures

Hydrogenation of carbon monoxide was carried out in a high pressure flow system equipped with a stirred slurry-bed reactor at 270°C and at 30 atm (1 atm=101 kPa). Syngas with a hydrogen-to-carbon monoxide molar ratio of 2 was fed to the bottom of the reactor through a nozzle and was allowed to react on the catalyst suspended in hexadecane. An ultrasonic generator was used to prepare a suspension of the catalyst prior to FT reaction. The experimental apparatus for the

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synthesis and the analytical procedures were reported previously⁹⁾.

2. 2. Catalysts

Ultrafine particles of Co and Co-M (M:Cr, Ti, Zr, Mn, K, Mg, etc.) were used as catalysts in the present work. The UFP catalysts were prepared by the method of chemical deposition in the liquid phase. An aqueous solution of NaBH₄ was added dropwise to an aqueous solution of CoCl₂ and another metal chloride. The solution was stirred until no evolution of hydrogen was observed. The precipitate was filtered and washed with water and then with methanol. After drying *in vacuo*, the catalyst was crushed into a fine powder in nitrogen atmosphere. The average particle size of UFP used here was determined to be in the range from 180 to 270 Å (1 Å=10⁻¹⁰ m) by TEM observations.

Precipitated Co-Cr/SiO₂ was prepared according to the method described by Anderson and co-workers¹³⁾. SiO₂ (surface area 81 m²/g, average pore size 486 Å, pore volume 0.98 ml/g) obtained from Fuji Davison Co., Ltd. was added to an aqueous solution of Co(NO₃)₂ and CrCl₃, and then an aqueous solution of Na₂CO₃ was added dropwise at 90°C. After filtration and washing, the product was finely crushed into powder and was reduced at 450°C for 10 h in hydrogen atmosphere.

Co-Cr/SiO₂ was prepared by impregnation of SiO₂ with an aqueous solution of Co(NO₃)₂ and CrCl₃, and the product was then activated using an aqueous solution of NaBH₄. After filtration and washing with methanol, the product was dried *in vacuo*. This catalyst will be abbreviated as Co-Cr/SiO₂(NaBH₄).

2. 3. Characterization

The number of catalytically active sites was calculated from chemisorptive uptakes of CO, assuming the reaction stoichiometry of CO/Co=1. Co-Cr/SiO₂ was evacuated *in vacuo* for 1 h and then heated to 200°C at a rate of 10 K/min. After reduction at 200°C for 2 h, the sample was evacuated for 1 h. CO chemisorption uptakes were measured at 25°C using a conventional statistic apparatus.

Reducibility of precipitated Co-Cr/SiO₂ was determined by temperature-programmed reduction. Co-Cr/SiO₂ 0.25 g was evacuated *in vacuo* at 100°C for 1 h. The sample was heated to 1000°C at a rate of 10 K/min in a stream of mixture of 90% He and 10% H₂ (120 Torr, 50 ml/min).

Temperature-programmed desorption of CO was carried out as follows. Co-Cr/SiO₂(NaBH₄) 5 g was reduced with hydrogen at 200°C for 2 h and was evacuated at the same temperature for 1 h. After cooling to room temperature, CO gas of

Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 35 g-cat. min CO-mol⁻¹.

Fig. 1 Catalytic Activities of Co-Based UFP for Slurry Phase FT Synthesis

230 Torr was adsorbed for 2 h and evacuated for 30 min. The sample was heated at a rate of 10 K/min in a stream of He (40 ml/min). The composition of effluent gases was monitored using of a mass spectrometer.

3. Results and Discussion

3. 1. Catalytic Performance of Co UFP

The results of space time yield (STY) of hydrocarbons on Co-based UFP catalysts in the initial 5 h of run are summarized in Fig. 1. Here, the Co UFP containing 2 wt% of another metal was used. Cr, Ti, Mn, and Zr were effective additives to enhance the catalytic activity of Co UFP. Among the UFP catalysts tested, Co-Cr showed the highest catalytic activity, and the STY of hydrocarbons of this catalyst was about 2 times as large as that of Co UFP catalyst. As shown in the figure, Co-Cr UFP was most selective for longer chain-hydrocarbon production among the catalysts tested. The selectivity of Co-based UFP for CO₂ was low, and that for hydrocarbons was higher than 95%. Selectivity of Co UFP catalyst for C₅⁺ hydrocarbons increased from 62.8 to 70.4% by addition of Cr but selectivity for methane decreased from 18.4 to 12.6%. Co-Mn and Co-Ti UFP catalysts provided product distributions similar to those for Co UFP catalysts.

Figure 2 shows the variation in the activity of UFP catalysts with time on stream. Activity of Co-Mg UFP catalyst was rapidly deteriorated with time on stream, although it exhibited high initial catalytic activity. Activities of Co-Cr, Co-Ti, and Co-Mn UFP catalysts scarcely changed at least for 5 h.

Co and Co-Cr UFP catalysts had a nonporous structure and the BET surface areas of 24.8 and 38.7 m²/g, respectively, in accordance with the

○, Co; △, Co-Cr; □, Co-Mn; ●, Co-Ti; ■, Co-Mg; ▲, Co-V UFP. Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 35 g-cat. min CO-mol⁻¹.

Fig. 2 Variation in the Level of CO Conversion with Time on Stream

Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 35 g-cat. min CO-mol⁻¹.

Fig. 3 Effect of Cr Content on the STY of Hydrocarbons on Co-Cr UFP Catalyst

average particle sizes of 266 and 180 Å as determined by TEM observations. High activities of these catalysts seem to be related to their large surface areas.

Further investigations were performed using the Co-Cr UFP catalyst which exhibited the highest activity and selectivity for C₅⁺ hydrocarbons production. The relation between activity and content of Cr is shown in **Fig. 3**. The catalytic activity of Co-Cr UFP increased with increasing content of Cr, and it attained a maximum at about 2 wt%. Cr UFP was inactive for FT synthesis.

Fig. 4 shows the effect of Cr content on selectivity for methane and C₅⁺ hydrocarbons production. Selectivity for C₅⁺ hydrocarbons production became maximum when 2 wt% Cr was added.

Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 35 g-cat. min CO-mol⁻¹.

Fig. 4 Effect of Cr Content on the Selectivities of Co-Cr UFP for CH₄ and C₅⁺ Hydrocarbons

3. 2. Catalytic Performance of Co/SiO₂

Co-Cr UFP was very active for the slurry phase FT synthesis. It is difficult to characterize Co-Cr UFP because Co-Cr UFP is sintered easily in the gas phase. In order to study the effect of Cr addition, characterization was performed using precipitated Co-Cr/SiO₂ and Co-Cr/SiO₂(NaBH₄) catalysts.

First, we studied the effect of catalyst preparation method on the catalytic properties of Co/SiO₂. **Table 1** summarizes catalytic activity and selectivity of precipitated Co/SiO₂ and Co/SiO₂(NaBH₄). Precipitated Co/SiO₂ was inactive for this reaction when it was reduced at 400°C. 8.2% CO was converted on precipitated Co/SiO₂ reduced at 450°C. Reduction at temperatures higher than 450°C lowered the catalytic activity. Co/SiO₂(NaBH₄) exhibited a higher catalytic activity than that of precipitated Co/SiO₂. Selectivity of Co/SiO₂(NaBH₄) for methane production was low compared with that of precipitated Co/SiO₂. At further investigations, precipitated Co/SiO₂ catalysts were reduced at 450°C.

Figure 5 shows the effect of Cr addition on activities of precipitated Co/SiO₂ and Co/SiO₂(NaBH₄) catalysts. Activities of both catalysts were enhanced by addition of Cr, and they reached a maximum when 10 wt% Cr was added. In the case of UFP catalyst shown in **Fig. 3**, Co-Cr UFP containing 2 wt% Cr exhibited the highest catalytic activity. The difference between UFP and supported Co catalysts can be explained as follows: Co UFP is effectively modified by Cr addition, while in the case of SiO₂-supported Co catalyst, both Co and SiO₂ react with the Cr added.

Table 1 Catalytic Activities and Selectivities of Precipitated Co/SiO₂ and Co/SiO₂(NaBH₄)

Catalyst		Precipitated Co/SiO ₂			Co/SiO ₂ (NaBH ₄)
Reduction temperature	[°C]	450	500	600	—
%Conversion of CO		8.2	7.1	4.1	14.2
STY	[g g-cat ⁻¹ h ⁻¹]				
Hydrocarbons		0.45	0.08	0.14	0.82
Oxygenates		0.008	0.002	0.002	0.017
CO ₂		0	0	0	0.133
Selectivity	[C-%]				
Hydrocarbons		98.8	98.5	99.1	93.7
Oxygenates		1.2	1.5	0.9	1.2
CO ₂		0	0	0	5.1
Distribution of products	[C-%]				
C ₁		47.5	44.2	47.1	25.5
C ₂		5.7	5.7	6.7	5.1
C ₃		12.3	10.8	11.7	10.5
C ₄		9.8	8.7	8.3	9.9
C ₅ -C ₁₁		18.4	19.6	15.7	27.2
C ₁₂ -C ₁₈		4.5	11.1	9.4	16.9
C ₁₉ ⁺		1.8	0	1.1	5.0
α		0.76		0.78	0.80

Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 100 g-cat.min CO-mol⁻¹. Content of Co, 10 wt%.

Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 100 g-cat. min CO-mol⁻¹. Content of Co, 10 wt%.

Fig. 5 Effect of Cr Content on the Catalytic Activities of Precipitated Co-Cr/SiO₂ (O) and Co-Cr/SiO₂(NaBH₄) (□)

Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 100 g-cat. min CO-mol⁻¹. Content of Co, 10 wt%.

Fig. 6 Effect of Cr Content on the Selectivity of Precipitated Co-Cr/SiO₂ Catalyst for CH₄ and C₅⁺ Hydrocarbons Production

Figure 6 shows the effect of Cr content on the selectivity of precipitated Co-Cr/SiO₂ catalyst for methane and for C₅⁺ hydrocarbons production. The catalyst of 10 wt% Cr content exhibited the lowest selectivity for methane production. We conclude from these results that the effect of Cr addition on catalytic performances of supported Co is the same as that of Co UFP.

To study the effect of Cr addition, chemisorptive uptake of CO was measured at 25°C using a conventional high vacuum static system. The number of active sites, determined from chemisorptive

uptake of CO, increased with increasing amount of Cr added, and the catalyst containing 10 wt% Cr exhibited the largest number of active sites. **Figure 7** shows the STY of hydrocarbons per active site as a function of Cr content. The STY of hydrocarbons per active site was almost constant, irrespective of the Cr content, and the results of STY on precipitated Co-Cr/SiO₂ and Co-Cr/SiO₂(NaBH₄) were 2.6×10⁻¹⁹ and 3.0×10⁻¹⁹ g·h⁻¹, respectively. These results indicate that activity increased by addition of Cr was related to the increase in the number of active sites.

Fig. 7 STY of Hydrocarbons per Active Site on Precipitated Co-Cr/SiO₂ (□) and Co-Cr/SiO₂(NaBH₄) (○) as a Function of Cr Content

Fig. 8 TPR Spectra of Precipitated Co and Co-Cr/SiO₂ Catalysts

Fig. 9 CO-TPD Spectra of Co-Cr/SiO₂(NaBH₄) (A) and Co-SiO₂(NaBH₄) (B) Catalysts

Figure 8 illustrates the TPR spectra obtained with precipitated Co-Cr/SiO₂ catalysts. Co/SiO₂ gave two peaks of hydrogen consumption at about 700 and 900°C. The amount of hydrogen consumption at high temperatures decreased and at low temperatures it increased with increasing Cr content. The TPR spectrum of Co-Cr/SiO₂ having 20 wt% Cr consisted of two peaks appearing at 300 and 600°C, and this catalyst was reduced at the lowest temperature among the catalysts tested. These results indicate that reducibility of Co was improved in the presence of Cr. These results allow us to conclude that there is a maximum number of active sites due to the promoting effects of Cr on reduction of Co and sintering of Co.

Chromium salts on SiO₂ supports are used industrially in the polymerization of ethene^{14),15)}. If polymerization activity of Cr affected the product distribution on supported Co-Cr catalysts, selectivity for C₅⁺ hydrocarbons production would increase with increasing amount of Cr

added. Thus, the change in selectivity for C₅⁺ hydrocarbon observed cannot be explained by polymerization activity of Cr.

Colley and co-workers¹²⁾ reported that incorporation of 2% Cr into co-precipitated Co-MnO catalyst shifted the selectivity toward higher hydrocarbons, and the selectivity remained almost constant on further addition of Cr. The shift in selectivity toward higher hydrocarbons seems to be caused by modification of Co surface with Cr. The surface properties of Co-Cr/SiO₂(NaBH₄) were evaluated by means of CO-TPD. Typical results are shown in Fig. 9. Peaks corresponding to the desorption of CO appeared on the Co/SiO₂(NaBH₄) catalyst at about 300 and 750°C, while desorption of CO₂ caused a single peak to appear at 300°C. This result indicated that CO dissociation took place on this catalyst. Co-Cr/SiO₂(NaBH₄) containing 10 wt% Cr produced desorption peaks at low temperatures compared with Co/SiO₂(NaBH₄). These results suggest that CO

Reaction conditions: temperature, 270°C; Pressure, 30 kg-G cm⁻²; H₂/CO, 2; W/F, 100 g-cat. min CO-mol⁻¹.
○, □, Co-Cr/SiO₂(NaBH₄); ●, ■, precipitated Co-Cr/SiO₂.

Fig. 10 Relation between Product Distribution and Size of Co Particles

binds more weakly to Co-Cr/SiO₂(NaBH₄) than to Co/SiO₂(NaBH₄) due to the effect of electron transfer from Co to Cr. It has been known that selectivity for higher-hydrocarbon formation increases with increasing strength of CO adsorption. The observed changes in the product distribution are not related to the adsorption behavior.

It was shown in our previous work¹⁶ that product distribution on Co UFP catalyst was dependent on the size of Co particles. **Figure 10** shows the relation between product distribution and Co particle size which was calculated from chemisorptive uptake of CO. The selectivity of precipitated Co-Cr/SiO₂ and Co-Cr/SiO₂(NaBH₄) catalysts for CH₄ production decreased and that for C₅⁺ hydrocarbons increased with decreasing size of Co particles.

4. Conclusion

The catalytic activity of Co UFP for slurry phase Fischer-Tropsch (FT) synthesis was increased by addition of Cr, Ti, and Mn among which Cr was found to be most effective. The space time yield (STY) of hydrocarbons on this catalyst was 14.2 g g-Co⁻¹ h⁻¹, and was about 2 times as large as that of Co UFP. Co-Cr UFP catalyst exhibited the

lowest selectivity for methane and the highest selectivity for liquid-hydrocarbon fuel among the catalysts tested. Similar results were obtained even on supported Co catalysts. Addition of Cr was found to increase the number of active sites due to the effect of promotional reduction of Co, resulting in a high catalytic activity. CO-TPD studies showed that CO was binding more weakly to Co-Cr/SiO₂(NaBH₄) than to Co/SiO₂(NaBH₄) due to the effect of electron transfer from Co to Cr. Selectivity for C₅⁺ hydrocarbons increased with decreasing size of Co particle, irrespective of the content of Cr.

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要 旨

液相 FT 合成用コバルト超微粒子触媒に対するクロムの添加効果

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Co 超微粒子 (UFP) 触媒を用いて液相フィッシャー・トロプシュ (FT) 合成を行った。Co と第 2 成分との複合 UFP 触媒の中で, Co-Cr UFP が最も高い活性を示した。Co-Cr UFP では, Cr 含有量 2 wt% で活性が最大となった。炭化水素の生成物分布も Cr の含有量とともに変化し, Cr 含有量 2 wt% でメタン選択率が最小となり, 液状油炭化水素の選択率が最大となった。SiO₂ 担持 Co-Cr 触媒では, Cr 含有量 10 wt% で UFP 触媒と同様な結果が得られた。

Cr の存在による活性および生成物分布の変化の原因を明らかにするため担持 Co-Cr 触媒の CO 吸着量を測定したところ, Cr 含有量 10 wt% で吸着量が最大となり, 活性点当たりの炭化水素の空時収率は Cr 含有量や触媒調製法に関係なくほ

ぼ一定となった。このことより, Cr の存在による活性の向上は活性点数の増加によると結論した。触媒の昇温還元測定で, Cr の存在により Co の還元がより低温で起こるようになることが示されたことから, Co-Cr 触媒で最大活性が存在するのは Cr の存在による Cr 還元率の増大とシントリングの促進という相反する効果のためと推測した。

一酸化炭素の昇温脱離測定の結果, Cr の存在により CO の吸着が弱められていることが明らかとなった。しかし, CO 吸着特性と生成物分布の変化の間には相関がみられなかった。以上のことより, Cr の存在による生成物分布の変化は Co 粒子径の影響のみを受けていると結論した。

Keywords

Fischer-Tropsch synthesis, Slurry phase reaction, Ultrafine particles, Cobalt, Chromium