Short Paper

Influence of Co Precursor and Pt Additive on Catalytic Performance of Highly Active Co/SiO₂-based Fischer-Tropsch Synthesis CatalystsNoriyuki YAMANE^{*1}^{*}², Kimihito SUZUKI^{*2}, Minghui TAN^{*1}, and Noritatsu TSUBAKI^{*1}[†]

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The effect of Co precursor and Pt additive on catalytic activity was investigated for Co/SiO₂ catalysts used for Fischer-Tropsch (FT) synthesis. FT reaction activity of Co/SiO₂ prepared using Co acetate as Co precursor was not high, but it was improved notably by adding small amount of Pt. It was found that small Co particles, which were hard to be reduced, were formed in the catalyst prepared using Co acetate. It is believed that the enhanced activity by Pt additive was mainly attributed to the improved reduction of small Co particles due to the added Pt. In addition, although the activity of Pt-Co/SiO₂ prepared using Co acetate as precursor was extremely high, but the selectivity of C₅₊ hydrocarbons was relatively low because of smaller Co particle size, and consequently there was no much difference on C₅₊ hydrocarbons productivity when the Co precursor was varied.

不純物含有量が少ない SiO₂ 担体に Co を 30 wt% 担持した高活性触媒について、Co 前駆体の影響、Pt 助触媒の効果を評価したところ、酢酸コバルトを前駆体として調製した Co/SiO₂ 触媒の活性は高くないが、Pt 助触媒を少量添加することで活性は飛躍的に向上した。Pt 助触媒の添加による活性向上は、還元されにくい小粒子径 Co が還元されたためと考えられる。しかし、酢酸コバルトを前駆体として調製した Pt-Co/SiO₂ 触媒の活性は著しく高いものの、C₅₊ 選択率は相対的に高くなく、C₅₊ 生産性は Co 前駆体によって大きな差は見られなかった。

Key Words

Fischer-Tropsch synthesis, Cobalt catalyst, Precursor, Pt addition, Gas-To-Liquid

1. Introduction

FT synthesis reaction is a synthesis method to produce clean liquid fuel from a mixed gas of carbon monoxide and hydrogen. Like the large-scale development technology in natural gas field in Qatar, etc., some commercial plants of GTL (Gas to Liquids) using Co-based FT catalyst are now operated¹⁾.

On the preparation of Co-based FT catalysts in industrial process, porous inorganic compounds such as Al₂O₃, SiO₂, TiO₂, etc. were always adopted as catalyst support and the catalyst was prepared by impregnation methods like incipient wetness, etc.. Catalyst activity of Co-based FT catalyst mainly depends on the loading amount of Co, additives, and content of alkaline metal or alkaline earth

metal which were inevitable impurities during catalyst production. It was reported that highly active catalyst could be obtained by lowering these impurities amount below around 100 ppm²⁾. The structure and chemical state of active Co metal particles on the catalyst could greatly influence the catalytic activity³⁾.

It is a huge advantage in reducing the catalyst cost by using highly active catalyst, because it can decrease the loaded amount of catalyst for commercial plant. In this study, influence of Co precursor and Pt additive on the catalytic activity of highly active Co/SiO₂-based catalysts with 30 wt% Co loading employing high-purity SiO₂ support was investigated, aiming at the application to a commercial GTL plant.

2. Experimental

2.1 Catalysts preparation

Catalysts were prepared by incipient wetness impregnation using Co nitrate (Co(NO₃)₂·6H₂O) or Co acetate (Co(CH₃COO)₂·4H₂O) as Co precursor. 30 wt% of Co

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was loaded on pure SiO₂ support containing Na: 105 ppm, Ca: 131 ppm, Mg: 4 ppm. As the adopted SV (space velocity) was rather high (W/F= 1.5 gh/mol), to achieve high CO conversion and high productivity, enhanced Co loading such as 30 wt% here was necessary. Drying treatment (393 K for 1 h) and calcination treatment (673 K for 5 h) were performed successively after Co loading. In the case of Pt addition, 0.1 wt% of Pt was loaded on Co/SiO₂ by incipient wetness impregnation using H₂PtCl₆ aqueous solution, and then drying and calcination were carried out. Reduction was performed in hydrogen flow at 673 K for 15 h and then passivation was carried out in 1%O₂/Ar balance gas at room temperature for 40 h. The catalyst nomenclatures were listed in Table 1. For example, Co/SiO₂ (Co acetate) meant the catalyst prepared using Co(CH₃COO)₂·4H₂O as the cobalt precursor.

2.2 Reaction of the catalysts

The reaction of FT synthesis was carried out in an autoclave with an inner volume of 300 mL. 1 g of catalyst and 50ml of n-hexadecane were charged into the autoclave. Thereafter, the flow rate of syngas (H₂/CO/Ar=60%/30%/10%) was adjusted to obtain W/F=1.5 gh/mol, while an agitator was rotated at 800 r/min under the condition of 503 K and 2.2 MPa. The composition of autoclave outlet gas was analyzed by gas chromatography equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). CO conversion, product selectivity, and C₅₊ productivity were calculated using the average value from 16 to 20 hour after reaction started.

2.3 Catalyst characterization

Reduction degree was measured by oxygen adsorption using Quantachrome AUTOSORB-1 gas sorption analyzer.

Prior to analysis, catalysts were reduced by hydrogen at 673 K for 1 h. H₂-TPR (Temperature-programmed reduction) was conducted on BELCAT II equipment. Samples of 0.1 g without reduction treatment were charged into the equipment and then pretreatment (673 K for 0.5 h) was carried out under argon gas flow. After cooling to room temperature, temperature was elevated from room temperature to 1142 K with a temperature ramp rate of 1 K/min under the 5%H₂/Ar gas. X-ray diffraction (XRD) was performed employing RINT 1500 (RIGAKU Co. Ltd.) recorded from 5 to 100° with a scan speed of 1°/min. Transmission electron microscopy (TEM) analysis was carried out using JEM2100F (JEOL Ltd.) equipped with an energy-dispersive spectrometer (JED2300T) under an accelerating voltage of 200 kV.

3. Results and discussion

FT synthesis reaction performances over Co/SiO₂-based catalysts were shown in Table 2. Co/SiO₂ (Co acetate) showed lower CO conversion of 58.8% than 72.3% of Co/SiO₂ (Co nitrate), indicating that Co precursor type had great influence on the catalytic activity of Co/SiO₂-based catalyst. Pt-Co/SiO₂ (Co acetate) showed the highest activity with the CO conversion of 78.7%, and the highest productivity of 2,365 g/kg-cat.h. Effect of 0.1 wt% of Pt additive was evaluated as 20% increase of the CO conversion and 600g/kg-cat.h improvement of the productivity. On the other hand, the CO conversion and productivity of Pt-Co/SiO₂ (Co nitrate) were slightly lower than those of Pt-Co/SiO₂ (Co acetate), but its C₅₊ selectivity was higher than that of Pt-Co/SiO₂ (Co acetate). As the CO conversion of Co/SiO₂ (Co nitrate) was 72.3%, effect of Pt additive was estimated as only 2% increase of CO conversion and 60 g/kg-cat.h improvement of productivity which was merely one-tenth the case of the catalysts prepared using Co acetate. This result indicated that catalyst activity was improved notably by Pt additive in the case of the catalyst prepared using Co acetate whereas catalyst activity was high enough without Pt addition in the case of the catalyst prepared using Co nitrate.

Reduction degree and particle size of Co particles on

Table 1 Nomenclature of catalysts

Catalyst	Co precursor
Pt-Co/SiO ₂ (Co acetate)	Co(CH ₃ COO) ₂ ·4H ₂ O
Co/SiO ₂ (Co acetate)	Co(CH ₃ COO) ₂ ·4H ₂ O
Pt-Co/SiO ₂ (Co nitrate)	Co(NO ₃) ₂ ·6H ₂ O
Co/SiO ₂ (Co nitrate)	Co(NO ₃) ₂ ·6H ₂ O

Table 2 Reaction performance comparison of catalysts

Catalyst	CO conv. (%)	Sel. (%)			Productivity (g/kg-cat.h)
		CH ₄	CO ₂	C ₅₊	
Pt-Co/SiO ₂ (Co acetate)	78.7	5.0	1.2	88.0	2,365
Co/SiO ₂ (Co acetate)	58.8	6.3	0.3	87.8	1,774
Pt-Co/SiO ₂ (Co nitrate)	74.0	3.8	0.5	92.2	2,322
Co/SiO ₂ (Co nitrate)	72.3	3.9	0.5	91.9	2,263

Reaction conditions: 503 K, 2.2 MPa, W/F=1.5 g/h/mol, H₂/CO=2

the catalysts were assumed to be the factors determining the catalyst activity since the active site of Co-base FT catalysts was Co metal. Therefore, reduction degree and particle size of Co particles were evaluated by oxygen adsorption, H_2 -TPR, XRD and TEM respectively.

Table 3 compared the reduction degree of the varied Co/SiO₂ catalysts. Reduction degree of the most active Pt-Co/SiO₂ (Co acetate) catalyst was not high, 57.9%. However, Co/SiO₂ (Co acetate) without Pt showed lowest reduction degree of 33.0%. 25% improvement was estimated for reduction degree of Co particles by addition of Pt on catalyst surface. On the other hand, compared with Co/SiO₂ (Co acetate), Co/SiO₂ (Co nitrate) showed a high reduction degree of 93.9% and enhanced slightly to 96.8% by Pt addition. Enhancement effect of reduction degree by Pt additive for Pt-Co/SiO₂ (Co nitrate) was only 3%. There is a good correlation between the improvement of reduction degree and the enhancement of activity by Pt additive. Pt-Co/SiO₂ (Co acetate) showed highest activity even if reduction degree of Pt-Co/SiO₂ (Co acetate) was low, compared with Pt-Co/SiO₂ (Co nitrate) and Co/SiO₂ (Co nitrate). It is considered that the surface area of Co metal in Pt-Co/SiO₂ (Co acetate) was higher than that of other catalysts because much small Co particles were formed as mentioned below.

To clarify the reason why the reduction degree of the catalysts prepared using Co acetate was low, TPR of these catalysts was conducted. The TPR profiles of the catalysts were given in **Fig. 1**. These profiles varied for catalysts prepared with different Co precursor: Co/SiO₂ (Co

acetate) exhibited the peak of reduction at 1055 K. After addition of Pt, peaks shifted to low temperature in both catalysts prepared using different Co precursors and the shift of peak was larger in the catalyst prepared using Co acetate specifically. Furthermore, the reduction temperature of Pt-Co/SiO₂ (Co acetate) was higher than that of Pt-Co/SiO₂ (Co nitrate). This means that Co particles of Pt-Co/SiO₂ (Co acetate) were difficult to be reduced in reduction process compared with the catalysts prepared using Co nitrate.

In order to investigate the structure of these catalysts after reduction, XRD was conducted. XRD patterns of the catalysts were depicted in **Fig. 2**. In the catalysts prepared using Co acetate, clear peaks of Co metal were not found. It was found that the peaks ascribed to CoO diminished and the peak width of 2 θ value from 42° to 45° grew to wide-angle by Pt addition. It indicated that reducing character of Co particles increased and the peak around 44.5° ascribed to Co metal appeared by addition of Pt. This result was accorded with the findings of oxygen adsorption and TPR. The estimation from the broadening of diffraction peaks at 42.7° according to Scherrer's equation gave crystallite size of 5.2 nm for CoO in Co/SiO₂ (Co acetate). In Pt-Co/SiO₂ (Co acetate), it was impossible to evaluate the crystallite size since there existed no independent peaks of Co metal, CoO, or Co₃O₄. On the other hand, a sharp peak appeared in the case of the catalysts prepared using Co nitrate. Crystallite size for Co metal was 14.5 nm for Pt-Co/SiO₂ (Co nitrate), 14.0 nm for Co/SiO₂ (Co nitrate), respectively. Compared with the catalyst prepared using Co acetate, Co particle size was almost triple in the catalysts prepared using Co nitrate. **Fig. 3** compares the TEM images of Pt-Co/SiO₂ (Co acetate) and Pt-Co/SiO₂ (Co nitrate). The TEM images demonstrate that small Co particles are dispersed well in Pt-Co/SiO₂ (Co acetate), while larger Co particles form aggregate in Pt-Co/SiO₂ (Co nitrate). **Fig. 4** demonstrates the EDS mapping of TEM image for Pt-Co/SiO₂ (Co nitrate) in order to elucidate the position between Pt and Co on the silica support.

Table 3 Reduction degree of catalysts

Catalyst	Reduction degree (%)
Pt-Co/SiO ₂ (Co acetate)	57.9
Co/SiO ₂ (Co acetate)	33.0
Pt-Co/SiO ₂ (Co nitrate)	96.8
Co/SiO ₂ (Co nitrate)	93.9

Fig. 1 TPR profiles of catalysts (5%/H₂/Ar, Ramp rate: 1K/min)

Fig. 2 X-ray diffraction patterns of catalysts

Fig. 3 TEM images of Pt-Co/SiO₂ (Co acetate): (a), and Pt-Co/SiO₂ (Co nitrate): (b) Fig. 4 EDS mapping of TEM image for Pt-Co/SiO₂ (Co nitrate)

Small amount of Pt existed on the location of Co particles, though Pt was barely detected in whole image. This finding discloses that Pt particles were contacted with Co particles. This Co particle size difference determined different C₅₊ hydrocarbon selectivity as listed in Table 2. It is reported that carbon chain growth probability was enhanced on larger Co particle size in FT synthesis⁴⁾. It is considered that readsorption of α -olefins was promoted on larger Co

particle. Consequently Co-based FT synthesis catalysts derived from nitrate precursor, with larger metallic cobalt crystallite sizes, exhibited higher C₅₊ hydrocarbon selectivity.

Being linked to carbon chain growth probability and C₅₊ hydrocarbon selectivity, Co particle size variation could be controlled by the interaction between Co precursor solution and catalyst support. Sintering of Co particles was unfavorable during drying, calcination and reduction processes after impregnation. If the interaction between Co precursor solution and catalyst support was strong, small Co particles would be formed. However, fine Co particles were hard to be reduced since these particles interacted with catalyst support strongly. One effective methodology to boost up the reduction degree of these fine cobalt oxide particles was implanting the co-existing noble metals such as Pt, Pd, to facilitate the H₂ spillover by these co-existing noble metals from syngas, quickly reducing the neighboring cobalt oxide species⁵⁾.

4. Conclusions

The effect of Co precursor and Pt additive on catalytic performance was investigated for FT synthesis

reaction over highly active catalyst, which loaded Co of 30 wt% on SiO₂ support containing low impurities. The catalysts using different Co precursors exhibited varied catalytic activity and Pt additive also had different influence on the activity of both catalysts. FT reaction activity of Co/SiO₂ prepared using Co acetate as Co precursor was not high, but it could be improved notably by adding a small amount of Pt. On the other hand, the activity of Co/SiO₂ prepared using Co nitrate was high even though the catalyst did not involve Pt, and the effect of Pt additive on this catalyst was negligible. It was found that much more small Co particles which were difficult to be reduced were formed on Co/SiO₂ (Co acetate). It is believed that Pt addition could facilitate the reduction of these small Co particles, hence improved the activity obviously. In addition, although the activity of Pt-Co/SiO₂ prepared using Co

acetate as precursor was extremely high, but the selectivity of C₅₊ hydrocarbons was relatively low, and there was no much difference on C₅₊ productivity when the Co precursor was different.

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