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# Synthesis of Petroleum Alternative Fuels by Fischer-Tropsch Synthesis on Cobalt-Platinum-Supported β-Zeolite Catalysts

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***Abstract*** - In this study, the effect of platinum (Pt) addition to cobalt (Co) supported -zeolite catalysts were examined for the synthesis of petroleum alternative fuels from syngas by Fischer-Tropsch reaction. Co-supported -zeolite catalysts (20 wt.% Co as $Co_3O_4$) were prepared by precipitation method and platinum was added by incipient impregnation method. Catalysts were characterized by various methods including $N_2$ adsorption (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), $H_2$ thermal programmed reduction ($H_2$-TPR), and transmission electron microscopy (TEM). Fischer-Tropsch (FT) synthesis was carried out over these catalysts at 230 °C and 1 MPa in a fixed-bed flow-type reactor. FT activity was improved by platinum addition to cobalt-supported β-zeolite catalyst. Cobalt existed in a state close to CoO before reduction, but a phase of metallic cobalt appeared after reduction. The addition of platinum lowered the reduction temperature, and fine cobalt particles that were difficult to reduce also became metallic cobalt, and the active sites increased, which led to improved activity for FT synthesis.

***Keywords*****:** Fischer-Tropsch synthesis, petroleum alternative fuels, Cobalt-Platinum-supported β-zeolite catalysts, nano-crystallites

## 1. Introduction

Petroleum resources are used all over the world as a power heat source, power generation, and raw materials for chemicals, but there is a risk that they will not be stably supplied in the future due to depletion and uneven distribution. Therefore, Fischer-Tropsch (FT) synthesis, which is a reaction to synthesize petroleum alternative fuels from syngas, is attracting attention. The advantages of FT synthesis include the availability of resources such as natural gas and biomass, which are less likely to be depleted, and the fact that the product does not contain sulphur and does not produce harmful substances when burned. However, the synthesis process is complex and requires many processes. Iron and cobalt are known as metals active in FT synthesis. Although cobalt is more expensive than iron, it has advantages such as long life, high activity at low temperatures, and the ability to be used on a carrier ]1]. The effects of the carrier include increasing the specific surface area of the catalyst metal, making the catalyst robust, and imparting effects that the catalyst metal does not have. Therefore, by supporting the catalyst metal on the carrier having the desired effect, the catalyst can have multiple functions. In our laboratory, we have studied the combination of a cobalt catalyst supported on various carriers and catalytic promoter, and aimed to develop a catalyst that can directly synthesize gasoline. As a result, it was found that the combination with the β-zeolite carrier can synthesize a liquid product close to the composition required for gasoline, and that the precipitation method is the optimal catalyst preparation method [2,3]. However, this catalyst had a low CO conversion rate and a small amount of liquid product was obtained.

Therefore, in this study, we tried to improve the catalytic activity by adding platinum, which has the function of promoting the reduction of the catalyst and increasing the formation of metal cobalt, which is considered to be the active species of the FT reaction [4]. The state of the catalyst after reduction was also analysed and evaluated in detail.

# 2. Experimental

## 2.1. Catalyst Preparation

Cobalt loading was performed using the precipitation method. Platinum was added by evaporation dry-solidity method. Commercially available β-zeolite powder ($SiO_2/Al_2O_3$ = 17.5) was calcined at 540 °C for 6 hours and ion exchange was performed with $NH_3OH_4$ solution. Ammonia water was added to a 5 wt% Co $(NO_3)_2 \cdot 6H_2O$ aqueous solution to which a predetermined amount of zeolite powder was added. After that, it was decanted to pH 7, washed, filtered, dried, and calcined. The obtained powdered cobalt-supported catalyst was sieved to 450-600 µm. Thereafter, a catalyst after granulation was added to a predetermined amount of dinitro di-ammine-platinum nitric acid solution, and the water was distilled away by an evaporator, and then dried and calcined. Drying was performed at 110 °C for 16 hours, and firing was performed at 500 °C for 1 hour. The cobalt loading was 20 wt% in terms of $Co_3O_4$, and the amount of platinum in terms of metal was 0, 0.5, 1, and 3 wt%.

## 2.2. Catalysts Characterization

The surface of the catalyst was observed using TEM (JEM-2100F, JEOL). The specific surface area and pore volume were measured by the nitrogen adsorption method with a nitrogen adsorption device (Gemini 2375, SHIMADZU). The metal dispersion and average particle size were measured by CO pulse measurement using BELCATII (Microtrackbel). The crystal structure was analyzed by an X-ray diffractometer (RINT2100, RIGAKU). X-ray photoelectron spectroscopy (XPS) was analyzed by JPS-9030 (JEOL). The reduction characteristics of the catalyst were measured by a constant speed temperature rise reduction method using a thermogravimetric analyzer (TGC-40M, SHIMADZU).

## 2.3. FT Synthesis Experiment

Reduction operation was performed at 400 °C in an $H_2$ atmosphere and under atmospheric pressure before FT synthesis (4 h). The FT synthesis experiment was performed at 1.0 MPa at 230 °C with a mixture of 0.5 g catalyst and $H_2/CO/N_2$ = 5/10/2, W/F = 2.2 (g·h/mol), and 6 h. The composition of the gaseous products ($C_1$-$C_4$) in the reaction was analyzed with GC-TCD (GC-8A, SHIMADZU) every 1 h (6 times in total). After the reaction, the carbon number distribution of the liquid product was analyzed by GC-FID (GC-8A, SHIMADZU) and the composition by GC-MS (GCMS-QP2010, SHIMADZU).

# 3. Results and Discussion

## 3.1. Evaluation of Catalytic properties

A list of prepared catalysts is shown in Table 1. These catalysts were observed by TEM (Figure 1). In all catalysts, there was a part of the fibrous crystallites and was agglomerated. These crystallites are considered to be a cobalt compound. Detailed observation revealed that there were many fine particles of 2-3 nm that were thought to be platinum.

Table 1 Properties of the catalysts

| Catalysts | Catalysts | Surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Dispersion (%) | Av. Crys. Size (nm) |
|---|---|---|---|---|---|
| $Co_3O_4$ 20 wt%, Pt 0wt% | 20Co-0Pt | 425 | 0.22 | 0.7 | 141.7 |
| $Co_3O_4$ 20 wt%, Pt 0.5wt% | 20Co-0.5Pt | 386 | 0.20 | 1.0 | 99.7 |
| $Co_3O_4$ 20 wt%, Pt 1 wt% | 20Co-1Pt | 383 | 0.20 | 0.8 | 122.0 |
| $Co_3O_4$ 20 wt%, Pt 3 wt% | 20Co-3Pt | 371 | 0.19 | 2.0 | 52.7 |

The physical properties of each catalyst, such as specific surface area and pore volume, are shown in Table 1. The specific surface area was 425 $m^2/g$ before platinum loading, but decreased with the increase in platinum loading. Since the pore volume was also reduced, it is inferred that some of the platinum is present in the pores of the catalyst. In addition, from the results of the metal dispersion and average particle size calculated by CO pulse measurement, it is considered that fine cobalt particles that are difficult to reduce were reduced by the addition of platinum, and the dispersion degree increased.

When the crystallinity of the catalyst was evaluated by XRD, almost no obvious peaks were observed other than the β-zeolite of the carrier, even though a fibrous part was observed in the TEM (data omitted). When platinum was added, fine peaks were observed at a position similar to the main peak of $Co_3O_4$, but no peaks consistent with platinum compounds were confirmed. From the above, it is considered that cobalt exists in an amorphous form, and that it is difficult to estimate the state of cobalt and platinum in detail with XRD.

Table 2 Binding energy analysis of the catalysts

| Catalysts | Binding Energy (eV) | | | | $Co^{3+}/Co^{2+}/Co^0$ |
|---|---|---|---|---|---|
| | Co $2p_{1/2}$ | Co $2p_{3/2}$ | Pt $4f_{5/2}$ | Pt $4f_{7\backslash2}$ | |
| 20Co-0Pt | 798.1 | 782.2 | - | - | 7.3/92.7/0 |
| 20Co-0.5Pt | 798.2 | 781.9 | 77.9 | 74.7 | 6.4/93.6/0 |
| 20Co-1Pt | 798.2 | 781.9 | 77.8 | 74.7 | 7.0/93.0/0 |
| 20Co-3Pt | 798.0 | 782.1 | 78.0 | 74.6 | 8.7/91.3/0 |

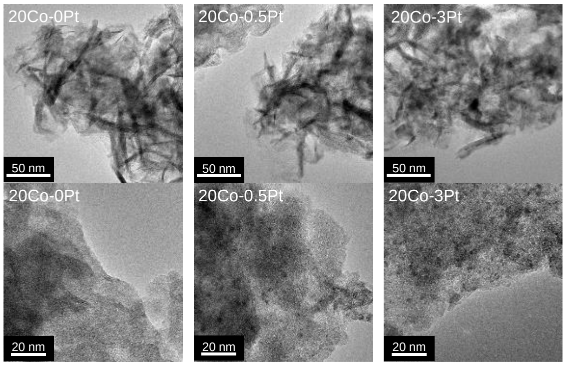

Fig. 1 TEM micrographs of the catalysts

Since it was difficult to evaluate the catalyst with XRD, the chemical states of cobalt and platinum on each catalyst surface were evaluated using XPS (Figure 2, Table 2). In the region of Co 2p, there was almost no difference in spectral shape depending on the presence or amount of platinum. The shape of the spectrum is similar to that of CoO, with satellite peaks appearing very large. When the abundance ratio of cobalt for each valence was calculated by waveform separation, the proportion of $Co^{2+}$ was about 90% in all catalysts, and only a small amount of $Co^{3+}$ was confirmed. Also, metallic cobalt did not exist. From these results, it is presumed that cobalt atoms exist in a state close to CoO on the catalyst.

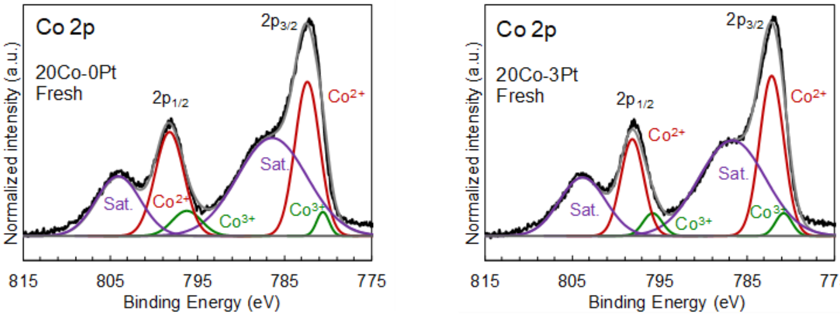

Fig. 2 XPS analysis of the catalysts

### 3.2. FT Synthesis Test Results

Table 3 shows the results of the FT activity test of each catalyst. The CO conversion rate was 25.3% before the addition of platinum, but the CO conversion rate improved to a maximum of 44.0% at 20Co-1Pt after the addition of platinum. The formation rate of liquid products ($C_{5+}$) was also improved from 17.2% to 29.0%. In addition, the liquid product decreased the olefin product and the paraffin product increased.

Table 3 FT synthesis results

| Catalysts | Conversion (%) | $C_{5+}$ Yield (%) | Composition (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | n-paraffin | i-paraffin | n-olefin | i-olefin | others |
| 20Co-0Pt | 25.3 | 17.2 | 24.9 | 55.9 | N.D.[a] | 10.7 | 8.5 |
| 20Co-0.5Pt | 32.6 | 20.8 | 28.5 | 55.5 | 0.8 | 8.9 | 6.3 |
| 20Co-1Pt | 44.0 | 29.0 | 30.3 | 56.8 | N.D.[a] | 7.5 | 5.3 |
| 20Co-3Pt | 37.7 | 25.6 | 28.6 | 59.3 | 1.1 | 5.5 | 5.4 |

[a] Not detected

### 3.3. Evaluation of the Catalysts Before and After Reduction

In order to examine the reason for the improvement of the CO conversion rate by the addition of platinum, the reduction characteristics were evaluated by temperature elevation hydrogen reduction measurement (data omitted). Before the addition of platinum, the reduction peak was 665 °C, but after the addition of platinum, the reduction peak was reduced to 570 °C, and it can be said that the reduction temperature could be lowered by the addition of platinum.

In order to confirm the effect of the decrease in reduction temperature on the chemical state of the catalyst during the FT reaction, the catalysts (20Co-0Pt, 20Co-3Pt) after reduction were analysed by XPS (Figure 3, Table 4). Before the addition of platinum, there was no metallic cobalt at all, but after the reduction, a phase of metallic cobalt appeared. The proportion of metallic cobalt increased when platinum was added. Since metallic cobalt is considered to be an active species in the FT reaction, the addition of platinum promotes reduction, which increases the proportion of metallic cobalt on the surface of the catalyst and improves the CO conversion rate.

For 20Co-3Pt, the chemical state of platinum on the catalyst before and after reduction was also analysed. The peak of Pt 4f5/2 shifted from 78.0 eV to 74.8 eV, and the peak of Pt 4f7/2 shifted from 74.6 eV to 71.3 eV (Table 4). From the peak position, platinum is considered to be in the state of $PtO_2$ before reduction, and it exists in the metallic state after reduction.

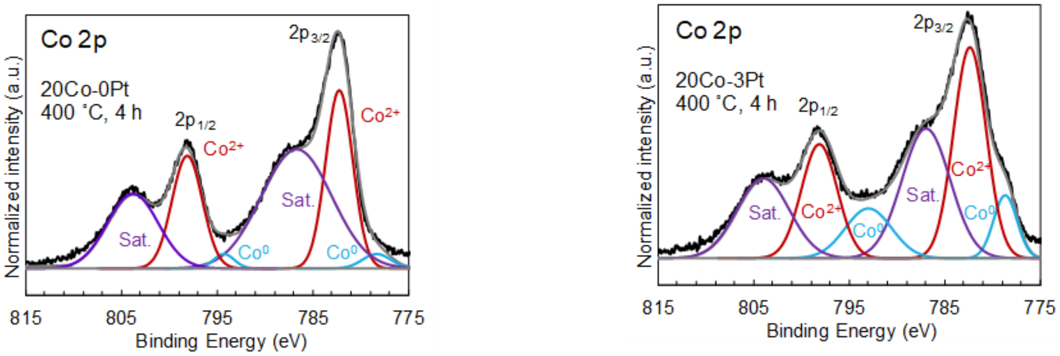

Fig. 3 XPS spectra of the catalysts after reduction

Table 4 XPS analysis of the post-reduced catalysts

| Catalysts | Binding Energy (eV) | | | | $Co^{3+}/Co^{2+}/Co^{0}$ |
|---|---|---|---|---|---|
| | Co $2p_{1/2}$ | Co $2p_{3/2}$ | Pt $4f_{5/2}$ | Pt $4f_{7\backslash 2}$ | |
| 20Co-0Pt (not red.) | 798.1 | 782.2 | - | - | 7.3/92.7/0 |
| 20Co-0Pt (red.) | 798.2 | 782.4 | - | - | 0/92.5/7.5 |
| 20Co-3Pt (not red.) | 798.0 | 782.1 | 78.0 | 74.6 | 8.7/91.3/0 |
| 20Co-3Pt (red.) | 798.4 | 782.7 | 74.8 | 71.3 | 0/82.4/17.6 |

## 4. Conclusion

FT activity was improved by platinum in a cobalt-supported β-zeolite catalyst.· Cobalt existed in a state close to CoO before reduction, but a phase of metallic cobalt appeared after reduction.·It is estimated that the platinum in the catalyst is mainly in the state of $PtO_2$, and after reduction, it became metallic.·The addition of platinum lowered the reduction temperature, and fine cobalt particles that were difficult to reduce also became metallic cobalt, and the active point increased, which led to improved activity.

## References

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