Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

A GC with an oxygen sensitive detector has been placed in operation.

Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

This has been accomplished and is currently being updated.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

7.1. Preparation of Promoted Cobalt Fischer-Tropsch Synthesis Catalysts

Introduction

With the discovery of more and more stranded natural gas resources, the development of cobalt based catalysts with high activity, stability and selectivity has become urgent. The common practice for the future commercial gas to liquid plant is believed to use promoted supported cobalt catalyst in a slurry phase reactor to optimize the diesel and wax productivity, The wax product then can be cracked into middle distillate or sold directly according to the local needs.

Intensive research has been done on the support, precursor, pretreatment and promoter effects on cobalt Fischer-Tropsch synthesis catalyst; however, the majority of these kinds of work were done in a fixed bed reactor. To study the effects of all the preparation parameters in the continuously stirring tank reactors will enable us to predict the behavior of the catalyst in a

bubble column slurry phase reactor. Therefore, the effect of promoters on the cobalt catalyst is studied in this work using a 1L CSTR reactor.

According to the results of Iglesia, the hydrocarbon productivity rate of cobalt catalyst only depends on its cobalt dispersion: the higher the dispersion, the higher the productivity rate. The support has no effect on the Fischer-Tropsch synthesis activity. The noble metal promoters' effect of increasing the activity is caused, in this view, by the promotion of reduction of cobalt oxide to cobalt metal. In previous work, we have prepared platinum and rhenium promoted alumina cobalt-catalysts and the activity was increased by the addition of small amount of Pt and Re. In this work, different loading of ruthenium was added to alumina supported catalyst to study the effect of Ru on the activity, deactivation rate and selectivity in 1L CSTR reactor.

Silica was considered to be a support that has a disadvantage for cobalt Fischer-Tropsch synthesis. Because in the presence of water, cobalt and silica can react and form cobalt silicate, thereby causing a rapid deactivation of the catalyst. Zirconia has been impregnated onto the surface of the silica support to retard the formation of the cobalt silicate during the reaction and it was proven to be very effective. Zirconia has also been added to the alumina support to increase the activity; however, the mechanism of the promotion effect has not been explained so far. In this work, zirconia was added to both silica and alumina support before the impregnation of cobalt and noble metal promoters.

It is mentioned in the patent literature that rare earth promotion of cobalt is beneficial to the Fischer-Tropsch synthesis. Several studies have found improved selectivity for longer chain hydrocarbons upon rare earth promotion of cobalt catalysts. In this report, the La promoted alumina supported cobalt catalyst was prepared and the effect of the La on the catalytic property of the catalyst is going to be defined.

Experimental

1. Co-Ru/Al$_2$O$_3$

The catalysts were prepared by the incipient wetness technique using Catalox B alumina (surface area 200m^2/g, pore volume 0.4cm^3/g). The cobalt precursor is Co(NO$_3$)$_2$6H$_2$O and the ruthenium precursor is Ru(NO)(NO$_3$)$_3$ XH$_2$O. The cobalt loading is 20wt% and the ruthenium loading are 0.2, 0.5, 1.0wt% respectively. The support was impregnated by a cobalt nitrate solution first, and the catalyst was calcined at 400oC in air. Ruthenium was added to the calcined cobalt-alumina and then the catalyst was dried and calcined again under flow air at 400^{0}C for 4hrs.

2. Co-Ru/ZrO$_2$-SiO$_2$

A silica support (Davisil 952) with a surface area of 300m^2/g and pore volume of 1.15cm^3/g was used. Zirconia was added to the silica surface in the form of ZrO(NO$_3$)$_2$ and the obtained catalyst were dried and calcined before the addition of cobalt and ruthenium. The zirconia loading was 10 wt.%, the cobalt loading is 20 wt.% and the ruthenium loadings were 0.2, 0.5, 1.0 wt.%, respectively.

3. Co/ZrO$_2$-Al$_2$O$_3$

The alumina support used was the same as for the Co-Ru/Al$_2$O$_3$, the zirconia precursor was ZrO(NO$_3$)$_2$ and it was added before cobalt. The obtained material then was dried and calcined before the addition of cobalt (cobalt loading was 15%), zirconia loading was 10%.

4. Co-La/Al$_2$O$_3$

Alumina support used was the same as Co-Ru/Al$_2$O$_3$, the La was added in the form of lanthanum nitrate hexahydrate with a La loading of 5% and the cobalt loading of 15%.

All of the above catalysts were prepared by the incipient wetness technique and the drying procedure was conducted in a rotary evaporator under vacuum. The catalytic properties of the catalysts are going to be obtained using a 1L CSTR reactor.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task 7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

8.1. Study of Re and Pt Promoted Cobalt/alumina Fischer-Tropsch Synthesis Catalysts in CSTR

Introduction

With the concept that stranded natural gas will be the main starting material for commercial Fischer-Tropsch synthesis in the short term, the importance of understanding the promoter effect of noble metals and the development of more stable and more active cobalt catalyst becomes more urgent. Bubble column slurry phase Fischer-Tropsch synthesis has been proven to have commercial success. In order to apply cobalt catalyst in the bubble column reactor, the catalyst should be tested in a continuously stirred tank reactor and then scaled up. Unfortunately, most research work on the promoter effect on cobalt Fischer-Tropsch synthesis catalysts was done in fixed-bed reactor in open literature. Ru, Re and Pt are the most commonly used noble metal promoters that have been added to the supported cobalt catalysts to increase the activity. In this work, Re and Pt promoted cobalt catalysts were prepared, characterized and the Fischer-Tropsch synthesis activity and selectivity were tested in 1 liter continuously stirred tank reactor. The results of the study suggested that both Re and Pt can increase the reduction degree of the cobalt and hence increase the activity of the catalyst. Re promoted catalysts have higher

initial Fischer-Tropsch synthesis activity than Pt promoted catalyst, but Pt promoted catalyst are more stable than their Re promoted analogues.

Experimental

The catalysts were prepared by the incipient wetness impregnation technique, the support material used was Catalox SB-200 alumina (Condea Vista) with a surface area of $200 m^2/g$ and pore volume of $0.43 g/cm^3$. The precursors for cobalt, platinum and rhenium are $Co(NO_3)_2 6H_2O$, $Pt(NH_3)_4(NO_3)_2$ and Re_2O_7, respectively. The cobalt loading for all the catalysts is 15 wt.%, three different loadings (0.2, 0.5, 1.0% wt%) of Pt or Re were added for the cobalt-alumina catalysts.

The catalysts were characterized by BET surface area, TPR, H_2- TPD, H_2 chemisorption, XRD and TEM methods. The degree of reduction and cobalt crystal size of the catalysts were calculated. Dispersion data from three different methods were compared. Fischer-Tropsch synthesis activity and selectivity of the unpromoted and different loadings of Re and Pt promoted catalysts were studied in a 1-liter continuously stirred tank reactor at 220^0C, 275 psig and $H_2/CO=2.0$.

Results and Discussion

1. Catalyst characterization

The results indicated that the presence of small amount of Re and Pt increased the dispersion of the metallic cobalt significantly due to the influence of the reducibility of the catalysts. The degree of reduction increased by addition of Re and Pt were probably caused by hydrogen spillover.

2. Fischer-Tropsch Synthesis

The activity (expressed as CO conversion) for both platinum and rhenium promoted catalysts are higher than the unpromoted analogue. The activity of rhenium promoted catalyst at a

space velocity of 2.0, 275psig and 220^0C was 72% at 46hrs time-on-stream and for the Pt

promoted catalyst was 60% at 45 hrs time on stream. However, the rhenium promoted catalyst

deactivated at a rate of 2.2% CO conversion per day, while the activity of platinum promoted

catalyst was stabilized at 74 hrs time on stream at a CO conversion of 51%, and after 430 hrs of

time-on-stream, the CO conversion was 48.5%. A linear correlation between the CO conversion

and the reciprocal of space velocity curve was observed for the Co(15%)-Pt(0.5%)/Al_2O_3

catalyst in the range of 0.125 to 0.5 (h g catalyst SL^{-1}). With increasing rhenium loading, the

hydrocarbon products became heavier indicating a product distribution effect of rhenium

promotion.
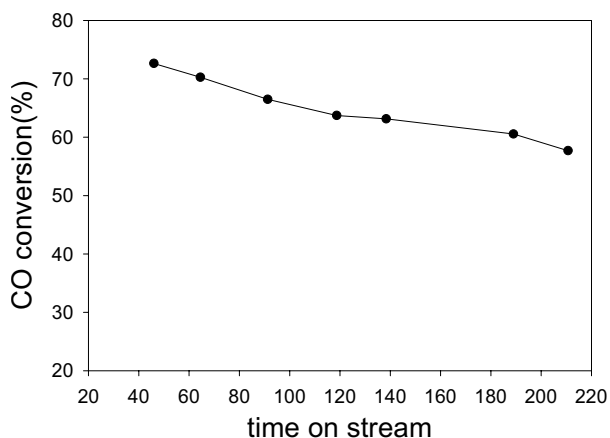
CO conversion as a function of time
on stream on Co(15%)-Re(0.2%)/Al_2O_3
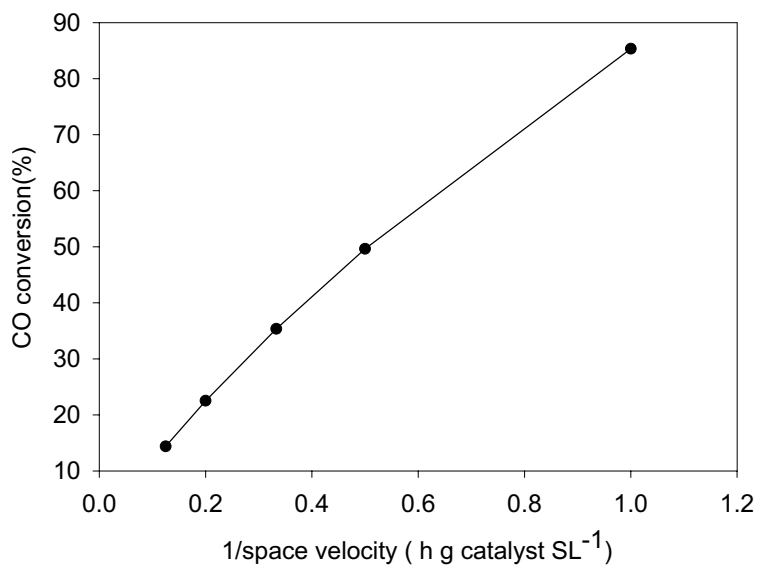
CO conversion as a function of reciprocal
flow rate for Co(15%)-Pt(0.5%)/Al$_2$O$_3$
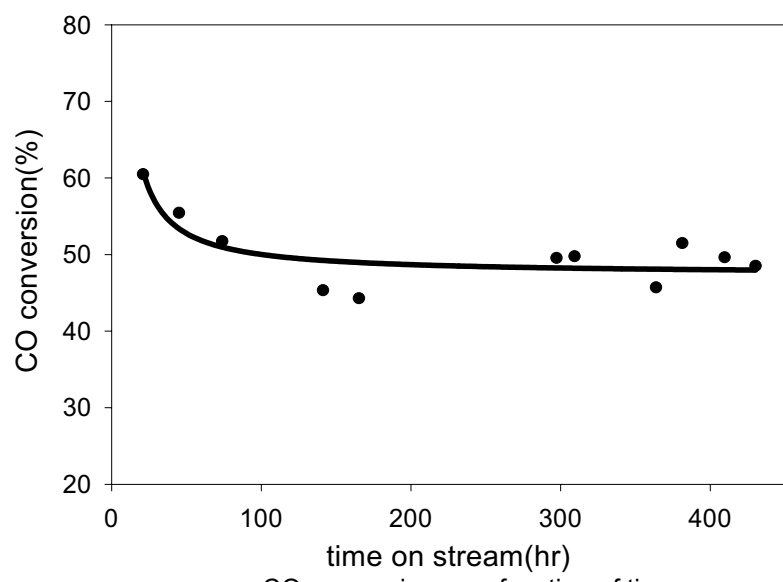
CO conversion as a function of time
on streamfor Co(15%)-Pt(0.5%)/Al$_2$O$_3$

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled activity to report.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

Task 11. University of California, Berkeley (Subcontract)

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H_2 on multi-component catalysts based on Fe as the active component.