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.

A.   Fischer-Tropsch Synthesis. Effect of CO pretreatment on a ruthenium promoted Co/TiO$_2$

ABSTRACT

The effect of pretreatment, using hydrogen or carbon monoxide, on the activity and selectivity of a ruthenium promoted cobalt catalyst [Ru(0.20wt%)/Co(10wt%)/TiO$_2$] during Fischer-Tropsch (F-T) synthesis was studied in a continuous stirred tank reactor (CSTR). The hydrogen reduced catalyst exhibited a high initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream, after which the catalyst deactivated slightly with time on stream. The carbon monoxide reduced catalyst reached steady state quickly and showed a lower activity and a good stability. Methane selectivity on the carbon monoxide reduced catalyst was 15 –20 % (carbon base), much higher than that on the hydrogen reduced catalyst (5 – 10%). Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have significant effect on the carbon monoxide reduced catalyst.

Key words : Cobalt, Ruthenium, Titania, Fischer-Tropsch synthesis, Synthesis gas conversion, CO pretreatment, Continuous stirred tank reactor.

Introduction

Pretreatment conditions used for supported cobalt Fischer-Tropsch (FT) catalysts often have significant effect on the catalyst activity, selectivity and lifetime (1-9). A number of researchers focused on the study of pretreatment of the catalyst with hydrogen, including the effects of calcination and hydrogen reduction temperatures. Calleja et al. (6) investigated the FT reaction over a Co/HZSM-5 catalyst, and found that the calcination and reduction temperatures did not have an effect on the catalyst activity. The results obtained by Rathousky et al. (8), however, revealed that the calcination and reduction temperatures have a significant effect on the catalytic properties of both Co/Al$_2$O$_3$ and Co/SiO$_2$ catalysts. The turnover frequency (TOF) for the F-T reaction decreased with increasing calcination temperature for both Co/Al$_2$O$_3$ and

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Co/SiO$_2$. However, the total reaction rate increased for Co/Al$_2$O$_3$ while it decreased for Co/SiO$_2$ (7-9). Belambe et al. (10) studied the pretreatment effects on the activity of a Ru-promoted Co/Al$_2$O$_3$ catalyst for the FT reaction. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst, but not on the TOF. The reduction temperature had only a negligible effect on the overall activity and TOF. A few studies on the effect of treatment with carbon monoxide or syngas for the supported cobalt catalysts has been reported. It has been reported that the supported cobalt catalyst pretreated with a gas containing carbon monoxide had increased activity and greater selectivity towards producing C$_5$+ hydrocarbons (11). Older work indicates that Co$_2$C is formed by low temperature activation with CO (12). Supported cobalt that were reduced in hydrogen, carburized with CO at 208°C and then hydrogenated at 208°C, the carbide was quickly converted to cobalt metal. Below about 240°C, treatment of cobalt catalysts with CO led to Co$_2$C with little, if any, free carbon.

The present work was undertaken to investigate the effect of carbon monoxide pretreatment on the titania supported cobalt catalyst. The results obtained have been compared with these of catalyst pretreated with hydrogen. The catalyst chosen for the present study is Ru(0.20 wt%)Co(10 wt%)/TiO$_2$. Our previous study (13) have shown that this catalyst had good catalyst activity and selectivity for Fischer-Tropsch synthesis.

Experimental

Catalyst preparation

The titania supported cobalt catalyst was prepared by pore volume impregnation of Degussa P-25 TiO$_2$ (72% anatase, 45 m^2/g, calcined at 673 K for 6 h before use) with a cobalt nitrate (Alfa) solution. The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium promoted catalyst was prepared by impregnating pretreated Co/TiO$_2$ with a solution containing ruthenium nitrosylnitrate (Alfa). The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium and cobalt contents were 0.20 and 10 wt% respectively, corresponding to a atomic Ru/Co ratio of 0.012.

Reaction system and procedure

A 1-liter autoclave, operated as a continuous stirred tank reactor (CSTR), was used for the slurry FT reaction. Analyses of the gaseous, liquid, and solid (at room temperature) products was conducted using a variety of both on- and off-line gas chromatographs.

The catalyst was pretreated with pure hydrogen or with pure carbon monoxide at different temperatures. The hydrogen activation was first conducted *ex-situ* and then *in-situ* according to the following procedure. The catalyst (about 15 g) was put in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh^{-1} (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh^{-1}, then increased to 573 K at a rate of 60 Kh^{-1} and kept 573 K for 16 h. The catalyst was transferred under a helium blanket to the CSTR to mix with 300 g of melted polyethylene (P.W. 3000). The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh^{-1} (298 K, 0.1 MPa). The temperature was increased to 553 K at a rate 120 K h^{-1} and maintained at this activation condition for 24 h.

The carbon monoxide activation was conducted *in-situ* in the CSTR according to the following procedure. Approximately 15 g of catalyst was mixed with 300 g of melted polyethylene (P.W. 3000) in the CSTR. The reactor pressure was increased to 1.68 MPa with carbon monoxide at a flow rate 30 NLh^{-1} (298 K, 0.1MPa). The reactor temperature was then increased to 523 K at a rate of 120 Kh^{-1}. These activation conditions were maintained for 24 h. In order to void any deposition of refractory carbon residues, a lower carbon monoxide pretreatment temperature (523 K) was chosen for this study.

After the activation period, the reactor temperature was decreased to 483 K and synthesis gas (2H$_2$/CO) was introduced to increase the reactor pressure to 2.35 MPa. The reactor temperature was then increased to 503 K at a rate of 10 Kh^{-1}. During the entire run the reactor temperature was 503 K, the pressure was 2.35 MPa, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas was 2 and 3 NL h^{-1} gcat.$^{-1}$ and the feed H$_2$/CO ratio was kept constant at 2. The conversion of carbon monoxide and hydrogen and the

formation of products were measured during a period of 24 h at each condition. Test duration was 210 h on stream for the hydrogen reduced catalyst or 350 h on stream for the carbon monoxide reduced catalyst. A common gas supply and carbonyl removal (using Pb-Al$_2$O$_3$) system was used for five CSTR's that were utilized with a variety of cobalt catalysts. Since the methane selectivity and activity stability of the other catalysts utilized in the other four reactors were normal, the feed should not impact the runs. Furthermore, since CO pretreatment has been utilized ns similar reactors for more than 100 runs without impact of metal deposition, the CO pretreatment should not impact the results. In this study, a PbO (20 wt.%)-Al$_2$O$_3$ trap for metal carbonyls was used. Prior work with an alumina trap led to deposition of iron on cobalt catalysts; however, following installation of the PbO-Al$_2$O$_3$ trap, chemical analysis showed that the iron contamination was eliminated.

Results and discussion

Catalyst activity

The synthesis gas conversion is a rough measure of the overall Fischer-Tropsch activity of a supported cobalt catalyst. The synthesis gas conversions (mol%) for RuCo/TiO$_2$ catalysts reduced with hydrogen and with carbon monoxide as a function of time on stream are shown in Figure 1 to illustrate the effect of pretreatment gas on catalyst activity. The space velocity used were 2 and 3 NL/gcat./h. Firstly, a space velocity of 2 NL/gcat./h was used. The hydrogen reduced catalyst exhibited a higher initial conversion of synthesis gas (73.5%), and it reached a steady state conversion at about 40 h on stream. After steady state, the catalyst deactivated slightly with time on stream. After 120 h on stream, the synthesis gas conversion had decreased to 66.7%, giving a deactivation rate was about 0.6% per day. When the space velocity was changed to 3 NL/gcat./h, the synthesis gas conversion decreased, reaching 45.0% at 140 h on stream.

The carbon monoxide reduced catalyst exhibited a very different catalytic performance compared with the hydrogen reduced catalyst. The synthesis gas conversion was lower and it reached a steady state value (32.0%) quickly. After 40 h on stream, the synthesis gas conversion increased slightly and then remained almost constant (34.0 %) with time on stream during 250 h.

When the space velocity was increased to 3 NL/gcat./h, the synthesis gas conversion decreased to 24.0%, lower that for the hydrogen reduced catalyst.

The rate of hydrocarbon production follows the same trend as the synthesis gas conversion, i.e., the hydrogen reduced catalyst exhibited a higher hydrocarbon production rate than the carbon monoxide reduced catalyst.

Catalyst selectivity

Methane selectivities for the catalysts reduced with hydrogen or with carbon monoxide (calculated as 100 x (moles of CO converted to CH_4)/(total moles of CO converted – moles of CO converted to CO_2)) as a function of time on stream are shown in Figure 2. Methane selectivity slightly changed between 15-20% with time on stream on the carbon monoxide reduced catalyst, and the values were higher than the hydrogen reduced catalyst (5-10%). The higher methane selectivity on the carbon monoxide reduced catalyst may be due to some cobalt carbide phase that was produced by the carbon monoxide reduction. However, the methane selectivity varied with synthesis gas conversion, and even a small change on synthesis gas conversion could influence methane selectivity. From Figure 3 it is seen that the same trend can be observed for the catalysts pretreated with hydrogen or with carbon monoxide; i.e. the methane selectivity decreased with increasing conversion for the two catalysts. As shown in Figure 3, the H_2/CO ratio of the exit gas remained essentially constant over the CO conversion range where the methane selectivity underwent significant changes. Thus, the different methane selectivity cannot be cue to different H_2/CO ratios. The alpha value, obtained from the Anderson-Schulz-Flory plot for the higher carbon number compounds, was essentially the same for the catalyst whether it was pretreated with H_2 or CO. Thus, the methane selectivity is not the result of widely varying FT selectivity.

One possible explanation is that a product is poisoning the methanation reaction relative to the FT reaction. Since water partial pressure increases with increasing CO conversion, it appears most likely that water selectively poisons the methane production. If this is the case, the most reasonable explanation is that there is a cobalt site that produces only methane, or low alpha FT products, that is poisoned by water. It does not appear that less methane could be

produced as the CO conversion increases in a single conventional pathway that follows Anderson-Schulz-Flory (ASF) kinetics.

Another possibility is that surface cobalt carbide is formed when the catalyst is exposed to only CO. If this is the case, the cobalt carbide sites would produce predominantly methane while the carbide-free cobalt sites would produce typical ASF products. Based on preliminary data produced when adding water to the feed, it appears that the explanation involving surface cobalt carbide is more likely to be valid.

C_5+ selectivity (expressed as a mass fraction of liquid and wax hydrocarbons in total hydrocarbons) exhibited a trend opposite to the methane selectivity. C_5+ selectivity on the hydrogen reduced catalyst was between 71.5 and 77.8%, higher than the carbon monoxide reduced catalyst (57.4 – 63.2%). However, similar alpha values were obtained for the two pretreatments.

Comparing the two pretreatment methods, the hydrogen pretreatment resulted in a higher Fischer-Tropsch activity, a lower methane selectivity and a higher C_5+ selectivity.

<u>CO regeneration effect</u>

In order to investigate the effect of carbon monoxide treatment on the used catalysts, synthesis gas was switched off after 140 h on stream for the hydrogen reduced catalyst (after 280 h on stream for the carbon monoxide reduced catalyst) and only pure carbon monoxide was passed in an attempt to regenerate the catalysts. The regeneration was carried out at reaction temperature of 503 K and a pressure of 1.68 MPa for 24 h. It was found that the carbon monoxide treatment (regeneration) led to a improved catalytic performance in a subsequent FT reaction for the hydrogen reduced catalyst. After regeneration, the synthesis gas conversion increased from 45.0 % to 58.0 % (at 3 NL/gcat./h) during the first 24 h and then gradually decreased to 52%. The methane selectivity firstly decreased from 9.8 to 5.6 % and then gradually increased. However, the carbon monoxide regeneration did not have significant effect on the carbon monoxide reduced catalyst and the synthesis gas conversion remained essentially constant (at 3 NL/gcat./h). The methane selectivity was not influenced by the regeneration (Figures 1 and 2).

Conclusions

The pretreatment gas (reductant) was found to have a remarkable effect on the performance of a ruthenium promoted cobalt catalyst during Fischer-Tropsch synthesis. The hydrogen reduced catalyst exhibited a higher initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream. The catalyst deactivated slightly with time on stream. The carbon monoxide catalyst reached steady state quickly, exhibiting lower activity and good stability. Methane selectivity for the carbon monoxide reduced catalyst was 15 –20 % (carbon basis), higher than that on the hydrogen reduced catalyst (5 – 10%). However, methane selectivity depends upon CO conversion and this can account for much of the differences in methane selectivity. Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have a significant effect on the carbon monoxide reduced catalyst.

Acknowledgement

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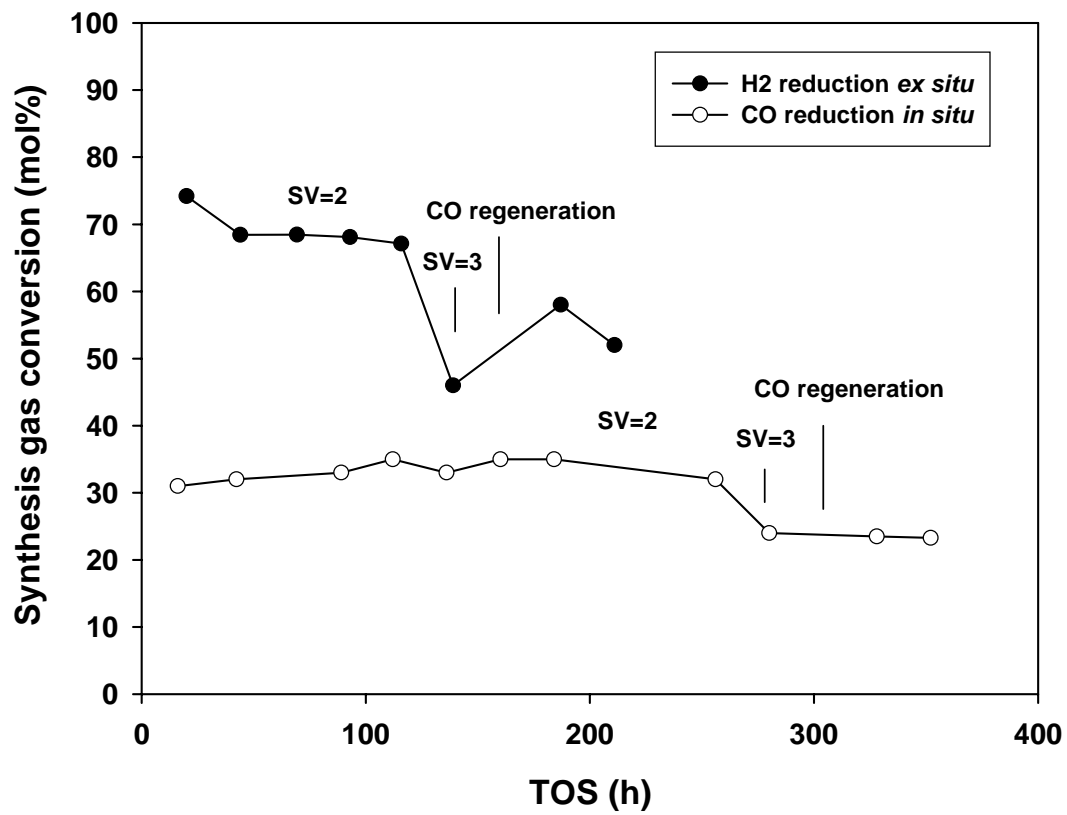13. J. Li, L. Xu, R. Keogh and B. H. Davis, *Catal. Lett.*, **70**, 127 (2000).

Figure 1. Effect of reduction gas on synthesis gas conversion of RuCo/TiO$_2$ catalyst
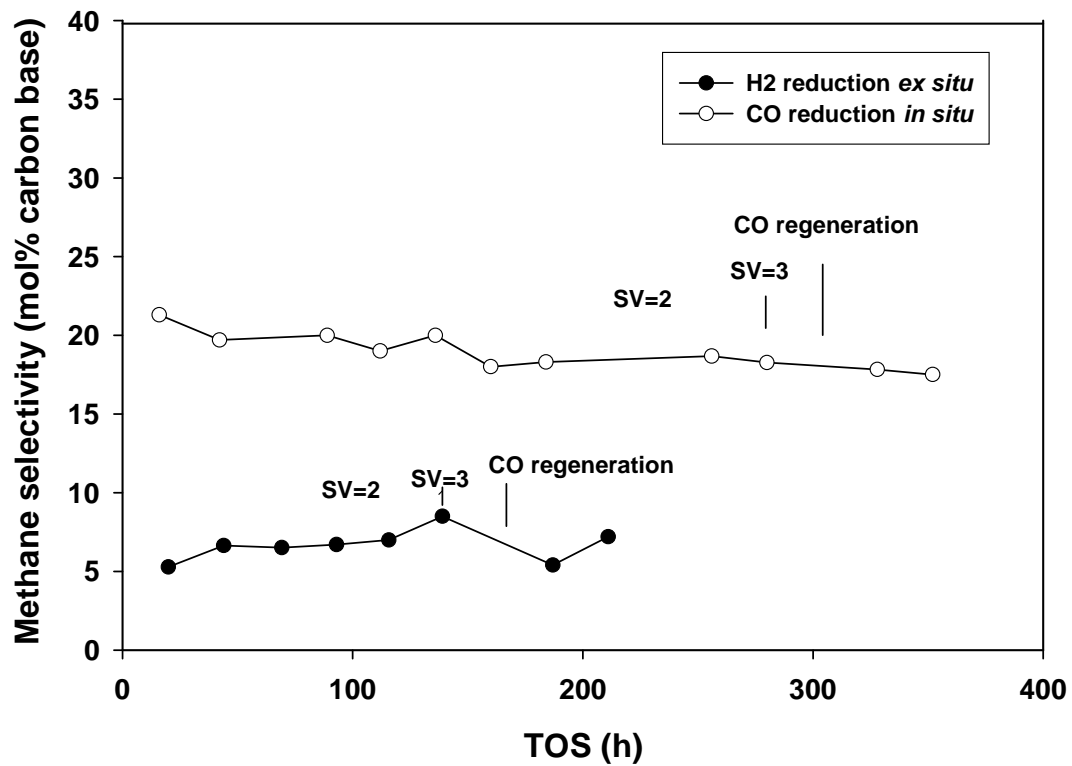
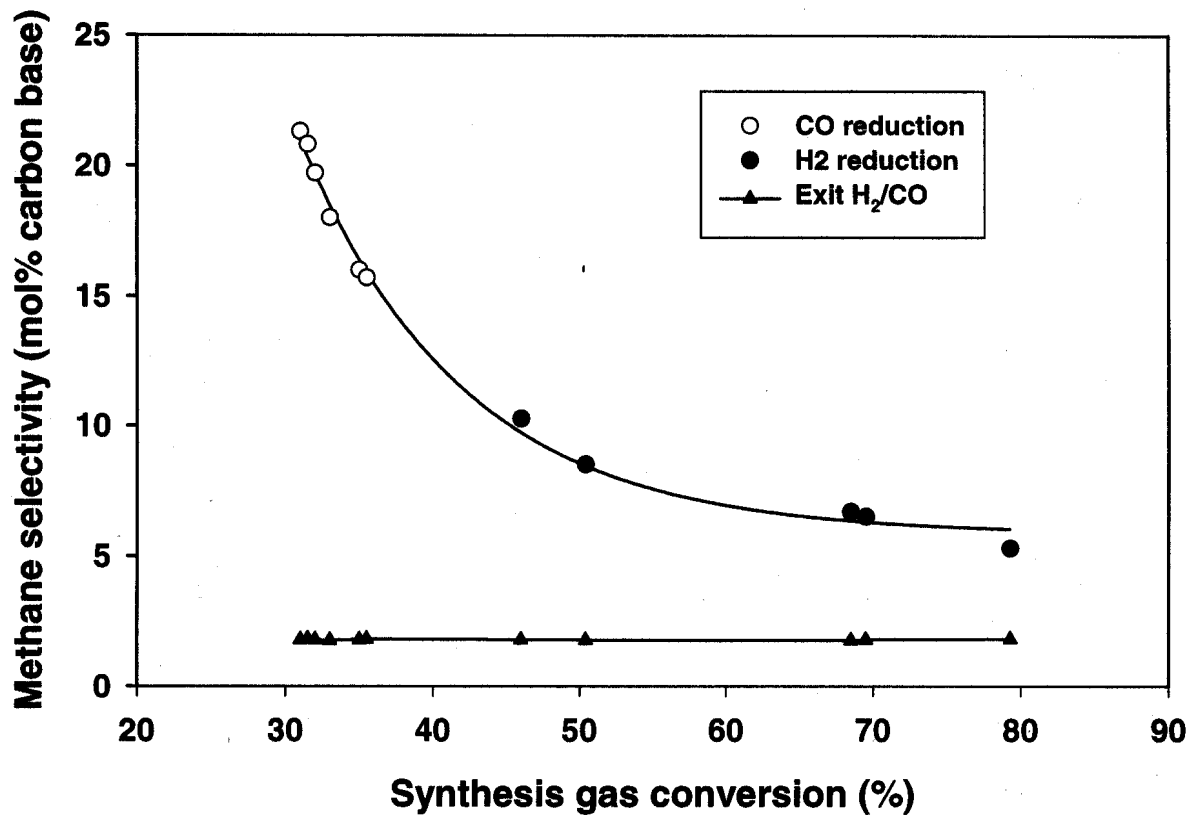**Figure 2. Effect of reduction gas on methane selectivity of RuCo/TiO$_2$catalyst**

Figure 3. Methane selectivity vs synthesis gas conversion

B.   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_2O_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 $Co(NO_3)_2 6H_2O$ and the ruthenium precursor is $Ru(NO)(NO_3)_3 XH_2O$. 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_2O_3

The alumina support used was the same as for the Co-Ru/Al_2O_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.

C.   Fischer-Tropsch Synthesis: Effect of Small Amounts of Boron, Ruthenium and Rhenium on Co/TiO$_2$ Catalysts

Abstract

The effect of the addition of small amounts of boron, ruthenium and rhenium on the Fischer-Tropsch catalyst activity and selectivity of a 10 wt% Co/TiO$_2$ catalyst has been investigated in a continuously stirred tank reactor (CSTR). A wide range of synthesis gas conversions has been obtained by varying space velocities over the catalysts. The addition of a small amount of boron (0.05 wt%) onto Co/TiO$_2$ does not change the activity of the catalyst at lower space times and slightly increases synthesis gas conversion at higher space times. The product selectivity is not significantly influenced by boron addition for all space velocities investigated. Ruthenium addition (0.20 wt%) onto Co/TiO$_2$ and CoB/TiO$_2$ catalysts improves the catalyst activity and selectivity. At a space time of 0.5 h-gcat./NL, synthesis gas conversion increases from the 50-54% to 68-71% range and methane selectivity decreases from 9.5% to 5.5% (molar carbon basis) for the promoted catalyst. Among the five promoted and non-promoted catalysts, the rhenium promoted Co/TiO$_2$ catalyst (0.34 wt% Re) exhibited the highest synthesis gas conversion, and at a space time of 0.5 h gcat./NL, synthesis gas conversion was 73.4%. In comparison with the results obtained in a fixed bed reactor, the catalysts displayed a higher Fischer-Tropsch catalytic activity in the CSTR.

Key words: Cobalt, Titania, Boron, Ruthenium, Rhenium, Fischer-Tropsch synthesis, Synthesis gas conversion, Continuously stirred tank reactor.

1. Introduction

Supported cobalt catalysts have been widely employed for Fischer-Tropsch (F-T) synthesis of long chain hydrocarbons from synthesis gas [1]. Cobalt is claimed to have certain advantages over iron as a catalyst, such as longer catalytic life time, less water-gas shift and production of a modified product. However, the activity of such catalysts still needs improvement. Variation of promoters is being considered as a means to reach this goal. It is well known that the activity of supported cobalt catalysts is increased by the addition of a small amount of ruthenium, and previous studies have indicated that ruthenium addition enhances the

reducibility of cobalt as well as the dispersion [2]. It is claimed to produce a synergistic effect with cobalt [3].

It is also known that many F-T catalysts suffer rapid and substantial loss of activity by poisoning in the presence of sulfur at ppm levels. There is, therefore, considerable interest in the development of more sulfur tolerant catalysts. One approach to remove small amounts of catalyst poisons is by using catalysts containing small amounts of complexes or elements that preferentially react with the poison. Iron, nickel and cobalt borides, which contain small amounts of boron, have been reported to be active and selective catalysts for the Fischer-Tropsch reaction [4-6] and, more importantly, these metal borates have also been shown to be significantly more resistant to sulfur poisoning in F-T synthesis [7].

In the present work, the effect of adding small amounts of boron, ruthenium and rhenium on the Fischer-Tropsch catalytic properties of titania-supported cobalt catalysts was studied. The incipient wetness impregnation (IWI) technique was applied to prepare catalysts and catalytic properties were evaluated in a continuously stirred tank reactor (CSTR). The results obtained in a CSTR were compared with those obtained in a fixed bed reactor.

2. Experimental

2.1. Catalyst preparation

The boron-modified TiO_2 carrier was prepared by pore volume impregnation of Degussa P-25 TiO_2 (72% anatase, 45 m^2/g, calcined at 673 K for 6 h) with a solution containing a small amount of boric acid (Aldrich). The sample was dried at 393 K for 16 h and then calcined in air for 6 h at 673 K.

Cobalt (10 wt%) was deposited on the boron-modified (or boron-free) TiO_2 carrier by pore volume impregnation with cobalt nitrate (Alfa) solution. Samples were dried at 393 K for 16 h and calcined at 573 K for 6 h before they were used.

The ruthenium or rhenium promoted catalysts were prepared by impregnating pretreated (10 wt%) Co/TiO_2 and CoB/TiO_2 with solutions containing ruthenium nitrosylnitrate (Alfa) or perrhenic acid (Alfa). The samples were dried at 393 K for 16 h and calcined at 573 K for 6 h before they were used. The boron, ruthenium and rhenium contents were 0.05, 0.20 and 0.34

wt% respectively, corresponding to atomic B/Co, Ru/Co and Re/Co ratios of 0.0273, 0.0117 and 0.0108.

2.2. Catalyst characterization

2.2.1. BET Surface Area Measurements

BET measurements were conducted using a Micromeritics Tri-Star system for all catalysts to determine the loss of surface area, if any, following loading of the metal. Prior to testing, samples were slowly ramped to 160°C and evacuated for 4 hrs. to approximately 50 m Torr.

2.2.2. Temperature programmed reduction

Temperature programmed reduction (TPR) profiles of freshly calcined catalysts were recorded using a Zeton Altamira AMI-200 unit which incorporates a thermal conductivity detector (TCD). Calcined fresh samples were first purged in flowing Ar to remove traces of water. TPR was performed using a flow of 20 ccm of 10%H_2/Ar mixture and referenced to Ar. The initial temperature was 323 K and the catalyts was ramped at 10 K/min to a final temperature of 1073K. Resulting profiles were normalized to the height of the main peak so that shifts in the peak positions could be ascertained.

2. 2. 3. Hydrogen chemisorption by temperature programmed desorption (TPD) and percent reduction by reoxidation

Hydrogen chemisorption was also measured using a Zeton Altamira AMI-200 unit. The sample weight in each case was 0.220 g. Catalysts were activated using pure hydrogen at 573 K for 10 hrs and cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon to prevent adsorption of weakly bound species, prior to increasing the temperature slowly to the activation temperature of 573 K. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectra were integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. The loop volume, determined by calibration with syringe injections of nitrogen in helium flow, was found to be 52

μL. Dispersion calculations were based on the assumption that the H:Co stoichiometric ratio was 1:1.

After TPD of hydrogen, the sample was reoxidized using pulses of oxygen in a He carrier gas at 573 K. Percentage reduction was calculated by assuming that the metal reoxidized to Co_3O_4.

For each sample, uncorrected dispersions and uncorrected particle size estimates were first determined assuming that the sample was completely reduced. The catalyst was fully oxidized when the peak corresponding to the oxygen pulse was observed in its entirity by the TCD, indicating no additional reaction with cobalt metal. Then, the percentage reduction of the sample was included in the calculation and corrected dispersions and particle size calculations were carried out. For particle size estimation, a spherical cluster morphology was assumed. Additionally, both dispersion and percentage reduction calculations were based solely on cobalt, and the promoter was not taken into account.

$D_{uncorrected}$ = No. of Co^o atoms / No. of Co atoms in sample

$D_{corrected}$ = No. of surface Co^o atoms / No. of Co^o atoms in sample

 = No. of surface Co^o atoms / (No. of Co atoms in sample)(fraction Co reduced).

2. 3. Reaction system and procedure

The catalyst (about 15 g) was reduced *ex-situ* in a fixed bed reactor with hydrogen at a flow rate of 60 NLh^{-1} (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh^{-1}, then increased to 573 K at a rate of 60 Kh^{-1} and kept at 573 K for 16 h. The catalyst was transferred under the protection of helium to a CSTR to mix with 300 g of melted Polywax 3000. The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh^{-1} (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h^{-1} and maintained at this activation condition for 24 h.

A 1-liter autoclave, operating as a continuously stirred tank reactor (CSTR), was used for the slurry FTS reaction. The FTS reactor system has been described earlier [8]. Separate mass flow controllers were used to added H_2, CO and inert gas at the desired rate to a mixing vessel

that was preceded by a lead oxide-alumina containing vessel to remove iron carbonyls. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. Products were continuously removed from the vapor and passed through two traps, one maintained at 373 K and then other at 273 K. The uncondensed vapor stream was reduced to atmospheric pressure through a pressure letdown valve. The flow was measured with a bubble-meter and composition quantified using an on-line GC. The accumulated reactor liquid products were removed every 24 hours by passing through a 2 µm sintered metal filter located below the liquid level in the CSTR. The contents of the 273 K and 373 K were combined, the hydrocarbon and water fractions separated, and analyzed by GC. The reactor wax sample was analyzed by a high-temperature GC to obtain a carbon number distribution for C_{20}-C_{80}.

After the activation period, the reactor temperature was decreased to 483 K and synthesis gas ($2H_2$/CO) was introduced to increase the reactor pressure to 2.35 MPa. The reactor temperature was then increased to 503 K at a rate of 10 Kh^{-1}. During the entire run, the reactor temperature was 503 K, the pressure was 2.35 MPa, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas was varied from 1 to 7 NL h^{-1} $gcat.^{-1}$ at a constant H_2/CO ratio of 2. The conversion of carbon monoxide and hydrogen and the formation of products were measured after at least a 24 h period at each condition.

3. Results and discussion

3.1. Catalyst Characterization

Results of surface area measurements by physisorption of nitrogen are reported in Table 1. Results show that the BET surface area for the 10% loaded Co catalysts on 45 m^2/g γ-Al_2O_3 were all close to 40 m^2/g. A weight % loading of 10% metal is equivalent to 13.3% by weight Co_3O_4. If the Al_2O_3 is the main contributor to the area, then the area of the Co/Al_2O_3 catalysts should be 0.867 ×45 m^2/g = 39 m^2/g, which matches very well the measured values. Therefore, the results in Table 1 are reasonable.

Figure 1 shows the TPR profiles for unpromoted and promoted Co/TiO_2 catalysts. For unpromoted catalysts, three peaks were observed. Reduction of Co_3O_4 to Co^0 passes through an intermediate phase, CoO and therefore the two-step reduction proceeds as follows:

$$1/3 \ H_2 + 1/3 \ Co_3O_4 => 1/3 \ H_2O + CoO$$

$$H_2 + Co => H_2O + Co^0$$
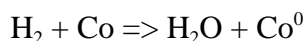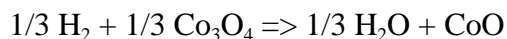
Therefore, in producing one mole of Co^0, one-third of a mole of H_2 is first consumed to produce CoO, and 1 mole of H_2 is consumed to produce the metal. We therefore anticipated that the ratio of the area of the first sharp peak with the remaining broad peak to be close to 0.33:1. Since bulk Co metal is thermodynamically stable after reduction in hydrogen at 623 K, the splitting of the peaks implies that the activation energy for the second reaction is higher. Because reduction is kinetically limited, the second sharp peak will contain, in addition to the first reaction, a small contribution from reduction of CoO to Co^0. This is most likely the reason why the calculated values in Table 2 are slightly higher than 0.33.

The low temperature peak was therefore assigned to reduction of Co_3O_4 to CoO while the higher temperature peaks corresponded reduction of CoO to Co. The high temperature broad peak was presumably due to reduction of species for which there exists a range of degrees of interaction of the metal oxide with the support. Addition of Ru shifted all peaks to lower temperatures. However, in comparison with the unpromoted catalyst, the promoter more significantly affected the low temperature peak, corresponding to reduction of Co_3O_4 to CoO, as observed in a previous study [3]. While the peak at 753 K for the unpromoted catalyst shifted to 636 K, a difference of 117 K, the low temperature peak shifted remarkably from 603 K to 473 K, a difference of 150 K. However, Re promotion only shifted the high temperature broad peak to lower temperature, while the lower temperature peak position remained unchanged. The enhanced reducibility is likely due to spillover of hydrogen from the reduced promoter to reduce cobalt oxide species, because the spectra are in line with the fact that the reduction of Re occurs at a higher temperature than Ru.

Addition of B did not enhance the reduction property of the catalyst, and in contrast, a notable increase in the reduction temperatures of all peaks was observed. However, addition of

both B and Ru to the catalyst resulted in an even more pronounced decrease in reduction temperature of all peaks to lower temperature than the catalyst with Ru promotion alone.

Addition of Ru lowered the activation energy barriers of both reactions, and shifted both peaks to lower temperatures, while addition of Re catalyzed primarily the second step. A comparison of the degree of reduction with time (Figure 2) supports the view that reduction occurs by nucleation and growth. By comparing the slopes of the lines for the promoted catalyst with the unpromoted catalyst, addition of Ru or Re likely increases the rate of nucleation of reduced sites on the cobalt oxide cluster, presumably by spillover of hydrogen from the reduced promoter metal.

Table 3 shows the hydrogen chemisorption data, where dispersion calculations were based on the assumption that the H:Co stoichiometric ratio was 1:1. Without taking into account the amount of Co left unreduced after reduction, estimates of dispersion are lower than the true value, leading to considerable overestimates of the resulting cluster size. Not surprisingly, percentage reduction values for samples reduced at 573 K were in line with the results of TPR. The boron promoted sample, which reduced at higher temperature in comparison with the unpromoted under TPR, showed the lowest percentage reduction value after treating with hydrogen at 573 K.

Likewise, samples promoted with Ru and Re showed much higher percentage reduction values in comparison with the unpromoted sample. The sample with the greatest fraction of its TPR spectra below 573 K, the RuCoB/TiO$_2$, sample, exhibited the highest percentage reduction value. The average sizes of the cobalt particles were calculated from the chemisorption data, considering the particles to be spherical and nonporous. The average particle size of the promoted catalysts are slightly smaller (~ 8.5 nm) compared to the unpromoted catalyst (~ 10.6 nm).

3.2. Catalyst activity

The synthesis gas conversion is a rough measure of the overall Fischer-Tropsch activity of a supported cobalt catalyst. A wide range of synthesis gas conversions has been obtained by varying space velocities over the boron and boron-free Co/TiO$_2$ catalysts. For a comparison, the

synthesis gas conversions have been measured at space velocities of 2 and 3 NL/gcat.h for the ruthenium and rhenium promoted catalysts. The synthesis gas conversions for the five catalysts are shown in Figure 3. At low synthesis gas conversion levels (space time < 0.33 h gcat./NL), Co/TiO_2 and CoB/TiO_2 catalysts exhibited about the same synthesis gas conversions. At higher space times (space time > 0.33 h gcat./NL), CoB/TiO_2 catalyst exhibited slightly higher synthesis gas conversion. The trends of synthesis gas conversion with space time for the two catalysts are very similar. The addition of 0.20 wt% ruthenium onto Co/TiO_2 and CoB/TiO_2 catalysts improved the catalyst activity. At a space time of 0.50 h gcat/NL, the synthesis gas conversions increased from 50.2 and 53.0% to 69.1 and 70.5% for the promoted catalysts, respectively. However, $RuCo/TiO_2$ and $RuCoB/TiO_2$ catalysts exhibited a similar synthesis gas conversion. This indicates that small amount of boron does not influence the Fischer-Tropsch activity of Co/TiO_2. The probable reason is that the number of active sites is not influenced significantly by the small amount of boron.

The rhenium promoted Co/TiO_2 catalyst ($ReCo/TiO_2$) showed the highest synthesis gas conversion among the five catalysts studied. At space times of 0.50 and 0.33 h gcat./NL, the synthesis gas conversions were 73.4 and 61.7%; these are higher than ruthenium promoted Co/TiO_2 and CoB/TiO_2 catalysts, and much higher than non-promoted Co/TiO_2 and CoB/TiO_2 catalysts. The observation that ruthenium and rhenium remarkably increased the activity of supported cobalt catalysts have been reported by other researchers [9-13]. However, few have provided an explanation for this. Kogelbauer et. al [2] investigated the effect of ruthenium on Co/Al_2O_3 Fischer-Tropsch catalysts and indicated that ruthenium enhanced the reducibility of the catalyst and therefore the number of exposed metallic cobalt sites, thus increasing the catalytic activity. A synergy effect for cobalt-ruthenium bimetallic was also used to explain the increased activities of ruthenium promoted Co/TiO_2 and Co/SiO_2 catalysts [3]. A recent paper indicated that ruthenium and rhenium increased the activity of supported cobalt catalysts because of the enhanced catalyst reducibility and dispersion [14]. Our catalytic activity, TPR and hydrogen chemisorption results show that the enhanced activity is due more to the increased reducibility of the catalyst. The average particle size changes very little after correcting for the percentage

reduction of cobalt. The slight decrease in particle size with promoter may be due to the reduction of smaller clusters that have a stronger interaction with the support.

Figure 4 shows that hydrocarbon production rate as a function of reciprocal flow rate. For the Co/TiO_2 catalyst, the hydrocarbon rate increased almost linearly with decreasing space time in the range studied. For the CoB/TiO_2 catalyst, however, the hydrocarbon rate increased first and then remained at a constant level of 0.2 g/gcat.h with decreasing space time. Compared with unpromoted Co/TiO_2 and CoB/TiO_2 catalysts, ruthenium and rhenium promoted catalysts exhibited higher hydrocarbon rates, with the rhenium promoted catalyst exhibiting the highest hydrocarbon rate. These trends are similar to those obtained for synthesis gas conversion as they should be since the impact of the higher conversion is offset by the lower amount of synthesis gas passed over the catalyst per hour..

3. 3. Catalyst selectivity

The hydrocarbon product distributions on non-promoted and promoted Co/TiO_2 catalysts have not been found to obey Flory kinetics (i.e., not a straight line) [3]. The methane and C_5+ selectivities are thus used to describe the Fischer-Tropsch selectivity. The methane selectivity, calculated as: 100 x (moles of CO converted to CH_4)/(total moles of CO converted – moles of CO converted to CO_2), as a function of reciprocal space velocity, is shown in Figure 5. The methane selectivity increased slightly with decreasing space time for Co/TiO_2 and $CoBTiO_2$ catalysts; however, for all the space times studied, the two catalysts showed very similar methane selectivities. Ru addition onto Co/TiO_2 and CoB/TiO_2 decreased the fraction of methane that was produced. At a space time of 0.5 h gcat./NL, the methane selectivity decreased from 9.5 and 9.6% to 6.1 and 5.5% (mole carbon base), respectively.

The methane selectivity on the rhenium promoted Co/TiO_2 catalyst was very similar to that of the ruthenium promoted catalysts and like the methane selectivity on the ruthenium promoted catalysts, it increased with decreasing the space time. Gaseous hydrocarbon selectivity (expressed as a fraction of C_2-C_4 hydrocarbons in total hydrocarbons, not shown) exhibited the same qualitative trends as methane selectivity.

The C_5+ selectivity (expressed as a mass fraction of liquid and wax hydrocarbons in the total hydrocarbons) of the five catalysts, as a function of reciprocal space velocity, is shown in Figure 6. The Co/TiO_2 and CoB/TiO_2 catalysts showed very similar C_5+ selectivities at all space times studied. At higher space times (> 0.33 h gcat./NL), C_5+ selectivity was constant; at the lower space times (< 0.33 h gcat./NL), C_5+ selectivity decreased with decreasing space time. Ru addition onto Co/TiO_2 and CoB/TiO_2 catalysts shifted the product spectrum to higher molecular weight hydrocarbons. At a space time of 0.5 h gcat./NL, the C_5+ selectivity increased from 64.5 and 66.8% to 74.5 and 78.0%. The rhenium promoted catalyst showed the highest C_5+ selectivity among five catalysts; at a space time of 0.5 h gcat./NL, C_5+ selectivity was 80.5%.

3.4. A comparison of Fischer-Tropsch activity in a fixed bed reactor with that in CSTR

Even though the reactors studied exhibited differences in their flow patterns, temperatures and pressures which will result in different phases present for the same catalyst as well as differences in product distributions, a comparison is displayed in Table 4 which points out the advantages of the enhanced mass/heat transfer characteristics of a CSTR. For Co/TiO_2 and CoB/TiO_2 catalysts, the product selectivities are very similar in the two reactors; however, Fischer-Tropsch reaction rates of catalysts obtained in the CSTR are two times higher than those obtained in the fixed bed reactor. It is emphasized that the results using the two types of reactors were obtained with different batches of catalyst although they were both prepared by the same person. None of the determined catalyst properties could explain the differences observed in the behavior of these catalysts in the two reactor systems. Obviously, less diffusion limitations and better gas solubilities in the liquid medium in the CSTR may explain the differences in the results from the two reactor systems [14]. For ruthenium and rhenium promoted Co/TiO_2 catalysts, the reaction rates obtained by us in the CSTR were higher than those obtained in fixed bed reactors. The methane selectivities obtained in CSTR were lower than those obtained in fixed bed reactors [14]. Iglesia et. al [3] used a low reaction temperature, which favored the formation of heavy products and, thus, they obtained a high C_5+ selectivity in the fixed bed reactor. Because the reaction conditions, especially pressure, are different, we can only make a

qualitative comparison of the catalytic properties of RuCo/TiO$_2$ and ReCo/TiO$_2$ in the two reactors.

4. Conclusion

The addition of a small amount of boron (0.05 wt%) onto Co/TiO$_2$ does not change the activity of the catalyst at lower space times (<0.33 h gcat./NL) and slightly increases synthesis gas conversion at higher space times (>0.33 h gcat./NL). The product selectivity is not significantly influenced by the boron addition for all the space velocities. Ruthenium addition (0.2 wt%) onto Co/TiO$_2$ and Co/B/TiO$_2$ catalysts remarkably improves the catalyst activities and selectivities. At a space time of 0.5 (SV=2 NL/gcat.h), CO conversions increase from 50.2 and 53.8 % to 68.4 and 70.5 % and methane selectivity decreases from 9.5 and 9.6% to 6.0 and 5.1% (carbon base). The rhenium promoted Co/TiO$_2$ catalysts (0.34 wt% Re) exhibits the highest synthesis gas conversion, and at a space time of 0.5 h gcat./NL, synthesis gas conversion is 73.4%. Addition of either Re or Ru improves considerably the percentage reduction of cobalt with only a marginal improvement in the average cobalt particle size. Comparing with the results obtained in the fixed bed reactor shows a higher Fischer-Tropsch catalytic activity in the CSTR.

Acknowledgment

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Table 1 BET Surface Areas		
Support/Catalyst	BET SA (m^2/g)	Ave Pore Size (nm)
Degussa P25 TiO$_2$	45	-
Co/TiO$_2$	38	11
CoB/TiO$_2$	40	14
RuCo/TiO$_2$	40	11
RuCoB/TiO$_2$	42	13
ReCo/TiO$_2$	43	12

Table 2	
Ratio of First Peak with Remaining Broad Peak in TPR	
Catalyst	Ratio of Area of First Peak to Remaining Broad Peak in TPR
Co/TiO_2	0.39
CoB/TiO_2	0.40
$RuCo/TiO_2$	0.36
$RuCoB/TiO_2$	0.38
$ReCo/TiO_2$	0.35

Table 3						
Dispersion and Reducibility of Unpromoted and Promoted Co/TiO$_2$ Catalysts						
Catalyst	μmoles H$_2$ Desorb	Uncorrected %D	Uncorrected Diam (nm)	% Reduction	Corrected %D	Corrected Diam (nm)
Co/TiO$_2$	42.8	5.05	20	52	9.70	11
CoB/TiO$_2$	37.4	4.40	24	38	11.6	8.9
RuCo/TiO$_2$	66.6	7.77	13	64	12.2	8.5
RuCoB/TiO$_2$	63.1	7.43	14	61	12.2	8.5
ReCo/TiO$_2$	65.6	7.73	13	61	12.8	8.1

Table 4

Fischer-Tropsch Synthesis on the Promoted Co/TiO$_2$ Catalysts

Catalyst	Pressure (Kpa)	Temp., (K)	CO Conv. (%)	Reaction Rate (10^{-4}molCO/molCo/s)	CH$_4$ (wt.%)	C$_5$+ (Wt.%)	Reactor
Co/TiO$_2$[a]	800	513	48.6	9.2	21.5	65.2	Fixed bed
CoB/TiO$_2$[a]	800	513	47.7	9.0	17.8	69.0	Fixed bed
RuCo/TiO$_2$[b]	2000	473	61.0	13.1	5.0	91.1	Fixed bed
RuCo/TiO$_2$[c]	100	493	< 5.0	3.3	27.7	---	Fixed bed
ReCo/TiO$_2$[c]	100	493	< 5.0	5.1	45.0	---	Fixed bed
Co/TiO$_2$[d]	2350	503	50.2	22.4	19.1	64.5	CSTR
BCo/TiO$_2$[d]	2350	503	53.8	24.0	16.2	66.8	CSTR
RuCo/TiO$_2$[d]	2350	503	68.4	30.5	13.9	74.5	CSTR
RuCoB/TiO$_2$[d]	2350	503	70.5	31.4	12.5	78.0	CSTR
ReCo/TiO$_2$[d]	2350	503	73.4	32.7	10.5	80.8	CSTR

A. Catalysts: Co/TiO$_2$, 10 wt.% Co; CoB/TiO$_2$, 10 wt.% Co, 0.05 wt.% B, from data in ref. [7].

B. Catalyst: RuCo/TiO$_2$, 11.6 wt.% Co, 0.14 wt.% Ru, from data in ref. [3].

C. Catalysts: RuCo/TiO$_2$, 12 wt.% Co, 0.5 wt.% Ru; ReCo/TiO$_2$, 12 wt.% Co, 0.75 wt.% Re, from data in ref. [13].
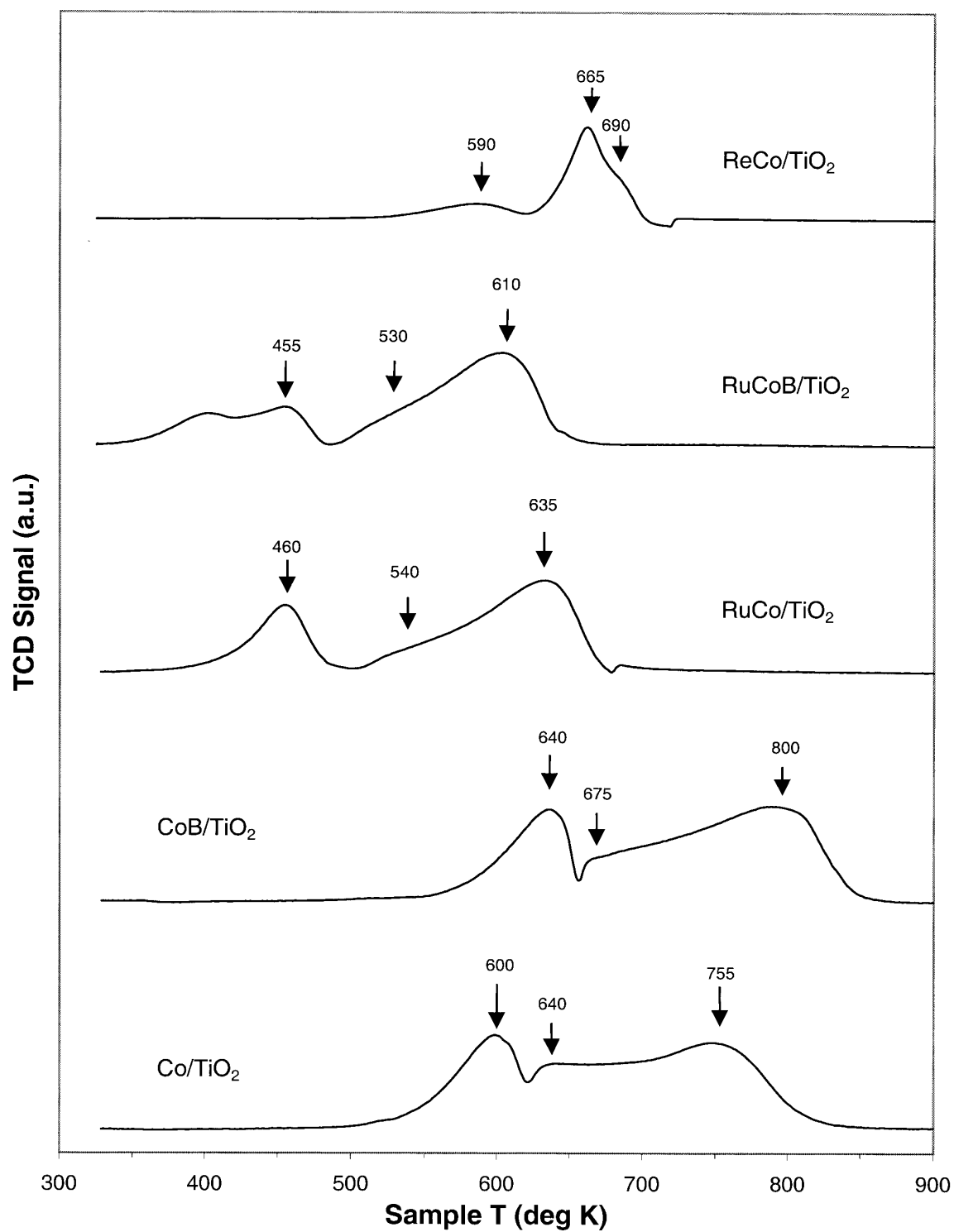
D. This study.

Figure 1. Temperature programmed reduction (TPR) profiles of promoted and unpromoted TiO_2 supported catalysts.
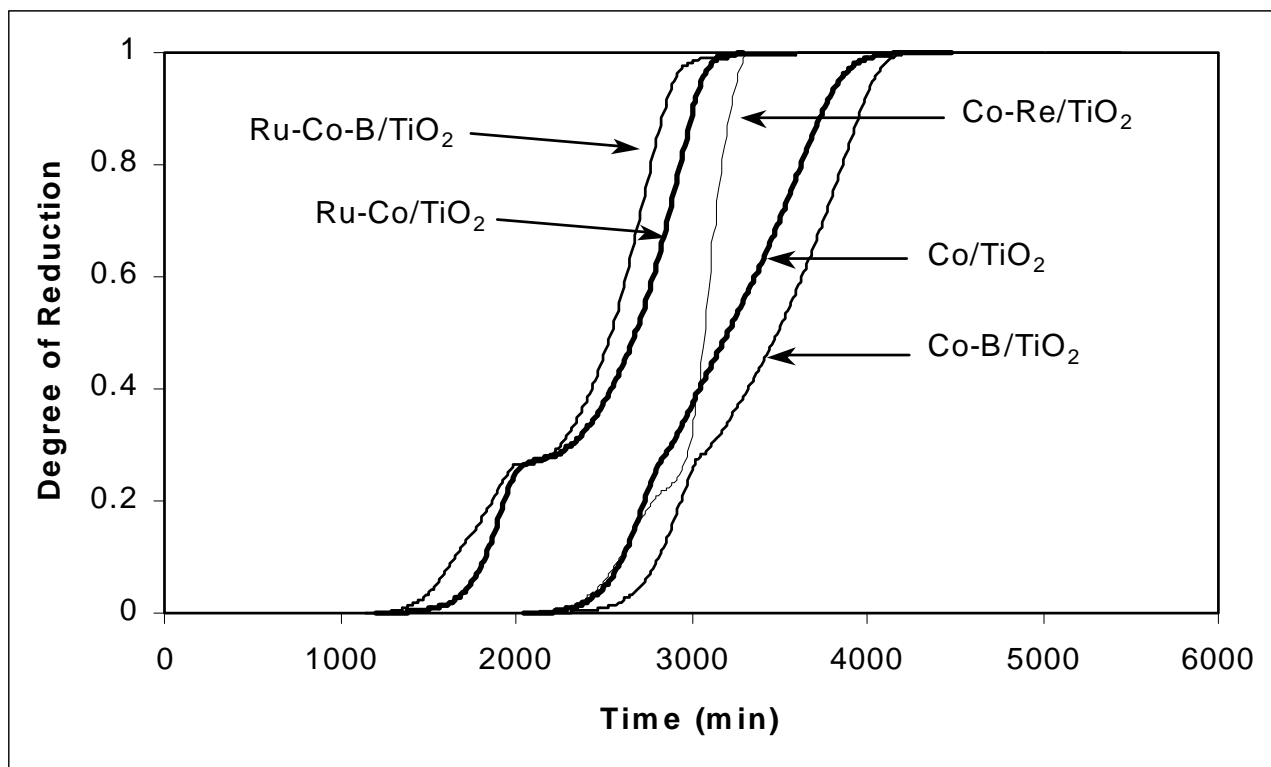
Figure 2. **Degree of reduction versus heating time for promoted TiO$_2$ supported catalysts (a value of 1.0 represents the extent of reduction after heating to 1073 K).**
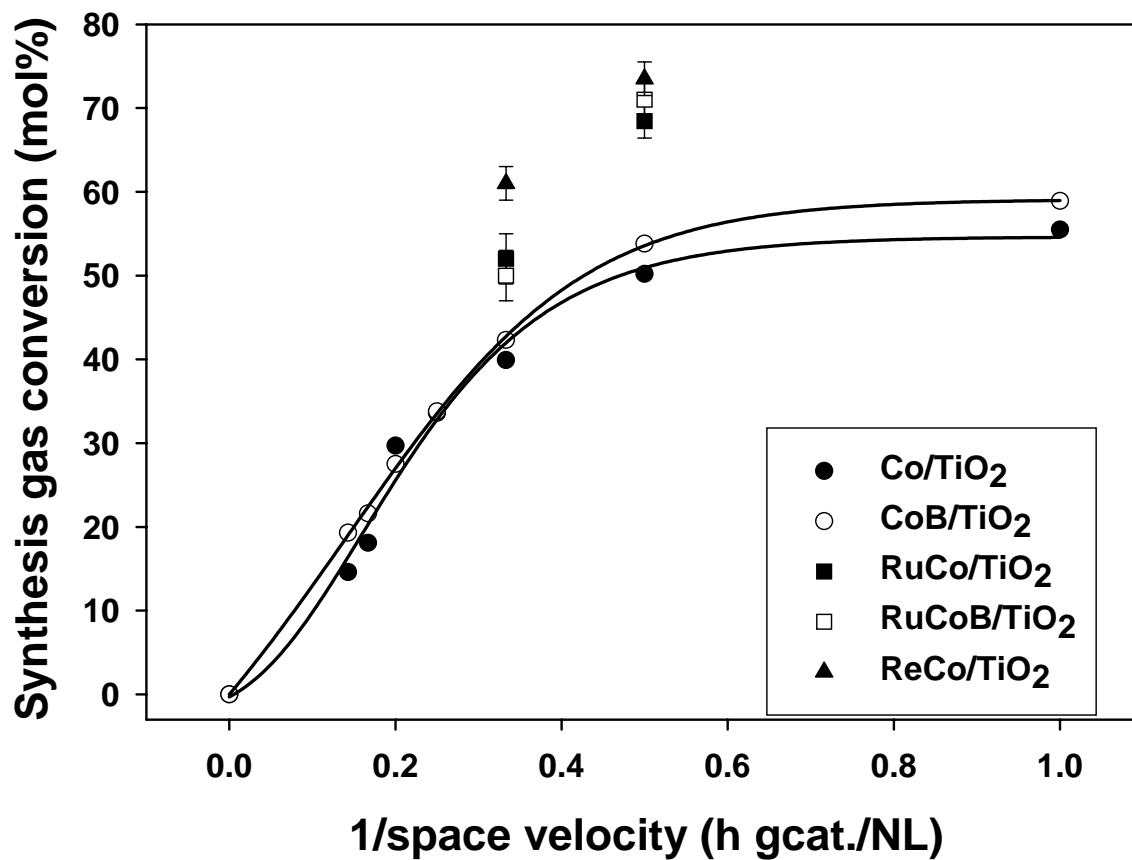
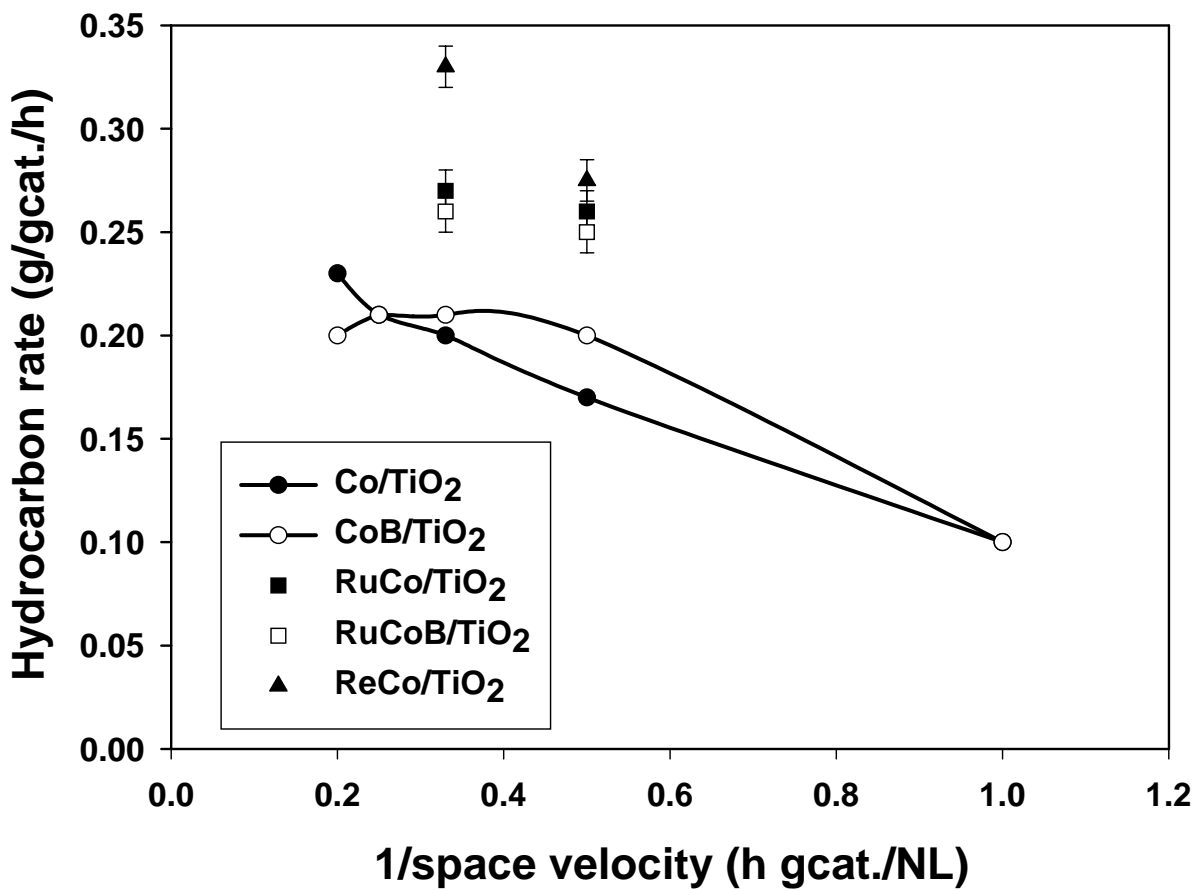**Fig. 3. Synthesis gas conversion as a function of reciprocal space velocity.**

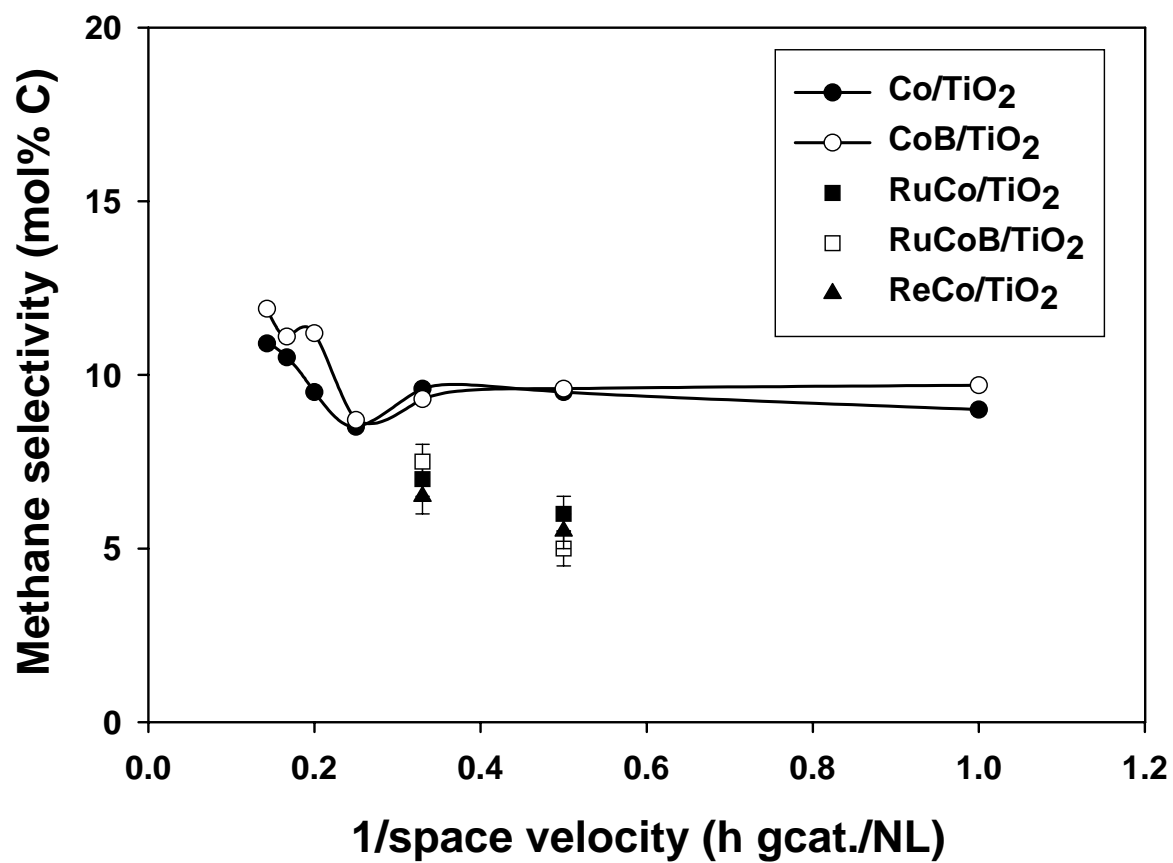**Fig. 4. Hydrocarbon production rate as a function of reciprocal space velocity.**

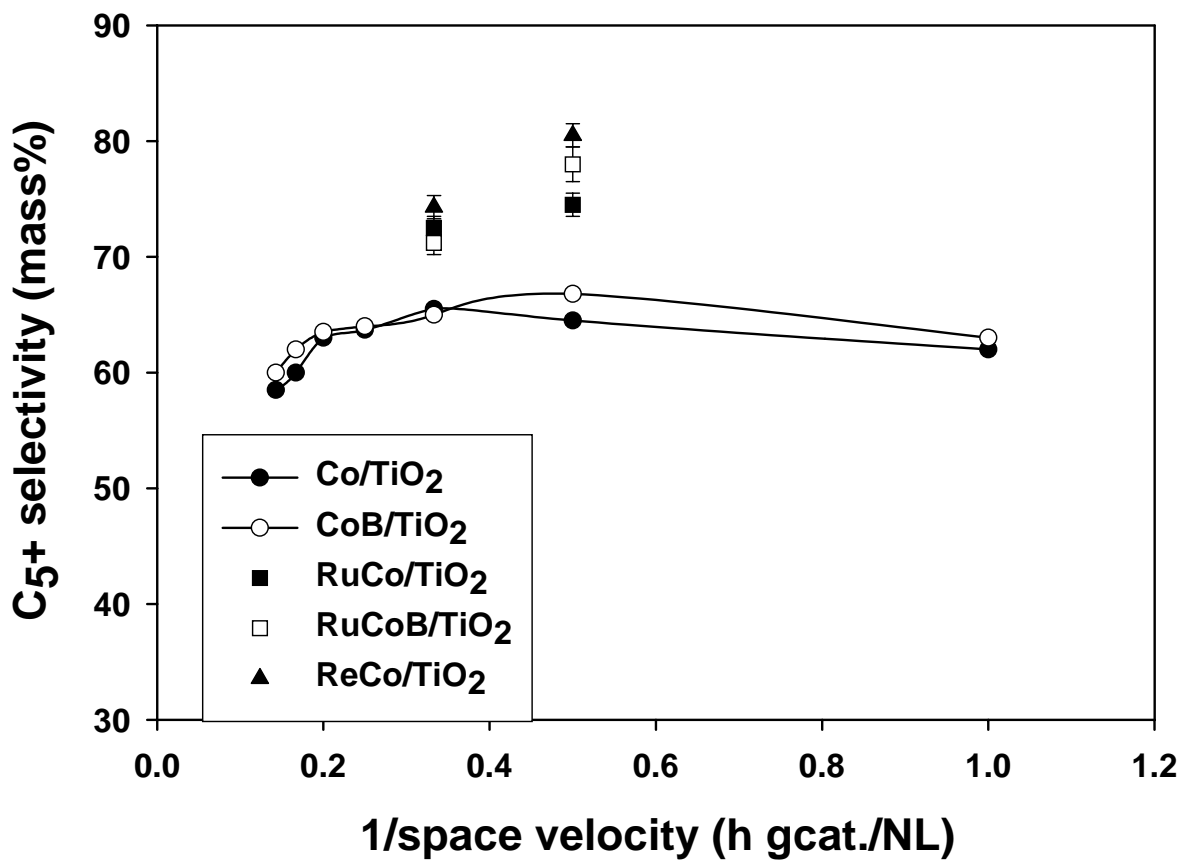**Fig. 5. Methane selectivity vs reciprocal space velocity.**

Fig. 6. C$_5$+ selectivity as a function of reciprocal space velocity.