Effects of Different Loadings of Ru and Re on Physico-Chemical Properties and Performance of 15% Co/Al$_2$O$_3$ FTS Catalysts

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ABSTRACT: *An extensive study of Fischer-Tropsch synthesis (FTS) on alumina-supported cobalt catalysts promoted with different amounts of ruthenium and rhenium is reported. Up to 2 wt% of promoters, are added to the catalyst by coimpregnation. The catalysts are characterized by different methods including: BET physisorption, X-ray diffraction, hydrogen chemisorption, and temperature-programmed reduction. The effect of the promoters on the reducibility of the cobalt oxide species, dispersion of the cobalt, and activity and selectivity of FTS is investigated. The Re enhances the reducibility of the CoO to Co^0 and small cobalt oxide particles with higher interaction with the support. However, Ruthenium was found to enhance the reducibility of Co$_3$O$_4$ to CoO and that of CoO to Co^0 and small cobalt oxide particles with higher interaction with the support. 1wt% Ru and 1.4wt% Re increased the activity of the catalyst by a factor of 2.8 and 2.5 respectively. Both promoters enhance the selectivity of Fischer-Tropsch synthesis towards the higher molecular weight hydrocarbons. However, the effect of Re is less pronounced.*

KEY WORDS: *Promoter, Fischer-Tropsch, Cobalt, Reducibility, Activity, C$_5$$^+$ Selectivity.*

INTRODUCTION

Interest in the Fischer-Tropsch synthesis (FTS) for hydrocarbon production from natural gas is increasing in viewpoint of clean fuel production. Due to low water gas shift activity and high chain growth probability, cobalt containing catalysts are among the best candidates for natural gas to clean liquid fuels (GTL) via Fischer-Tropsch synthesis. Cobalt also has higher activity in hydrogenation of CO, lower deactivation rate, and quite low price. While considerable commercial interest relating to FTS process on cobalt-based catalysts has been observed, much of the work has been proprietary and is not reported in the open literature. A large

number of patents have been issued in this area in the last two decades [1]. Any attempt to compare the performance of the various patented cobalt catalysts based on the claims is difficult since the catalysts were tested under different conditions. Various studies have been performed on the influence of promoters on cobalt-based catalysts supported on Al_2O_3, SiO_2 and TiO_2 [2 - 6]. *Iglesia* [7] reported that Turnover rates vary between 1.6×10^{-2} and 3.0×10^{-2} s^{-1} for a series of Co catalysts supported on Al_2O_3, SiO_2, TiO_2, SiO_2-modified TiO_2 and $MgCr_2O_4$, and the Fischer-Tropsch synthesis is a structure-insensitive reaction.

Supported Ru catalysts are excellent FTS catalysts, with high activity and chain growth probability. Indeed, supported Ru catalysts for FTS produce C_5^+ hydrocarbons with a selectivity of over 90 % at temperatures as low as 373 K. The application of ruthenium catalyst in FTS is restricted due to its high price. Therefore, usually a small amount of ruthenium is used as a promoter for the supported cobalt catalysts. Iglesia reported that addition of Ru to a cobalt catalyst tripled the activity of the catalyst and increased the C_5^+ selectivity from 84 % to 91 % [7]. Tsubaki et al. investigated the effect of promotion of Co/SiO$_2$ catalyst with small amounts of Ru, Pt, and Pd. They found that the Ru promoted catalyst had the highest CO hydrogenation rates. Ru enhanced the reducibility of the cobalt catalyst and enriched on the surface of cobalt particles [8].

Rhenium is also used as a promoter for supported FTS cobalt catalyst. *Vada et al.* and *O' Brien et al.* showed that, upon promotion of cobalt catalyst with 1 % Re, the apparent rates of catalysts increased, while the product selectivity remained unchanged [9,10].

Rygh et al. inspected the influence of 1 % Re promoter on the properties of 12 % Co/Al$_2$O$_3$. They found that Re could promote the reduction of cobalt, increase the amounts of bridged-type CO adsorption, and lower the reduction temperature of cobalt catalysts [11]. *Li et al.* reported that Ru and Re improved the catalytic activity and C_5^+ hydrocarbon selectivity of Fischer-Trposch synthesis [12]. Another study revealed that addition of 0 - 1 % Re to 15 % Co/Al$_2$O$_3$ catalyst, decreased the reduction temperature of cobalt but did not alter the dispersion and particle size significantly [13]. The added Re increased the apparent CO conver-

sion rate based on the catalyst weight, but turnover frequency remained unchanged. *Bertole et. al* [14] also indicated that Re did not affect the intrinsic activity or selectivity of the Co sites.

In the present work, a series of ruthenium and rhenium promoted catalysts with different amounts of Ru and Re loadings have been formulated. Due to the high price of the Ru and Re promoters, it is important to determine the optimum loading of the promoters for maximizing the availability of the active metal for catalyzing the Fischer-Tropsch reaction. All the catalysts were extensively characterized by different methods, including elemental analysis, BET physisorption, particle size distribution, X-ray diffraction, hydrogen chemisorption, and temperature programmed reduction. The catalysts were evaluated in terms of their Fischer-Tropsch activity and different products selectivity. A strong correlation between the activity and product selectivity with amounts of promoters and reducibility of the catalysts is observed.

EEPERIMENTAL
Catalyst preparation

All catalysts were prepared with 15 wt % cobalt on alumina as the support. The alumina was calcined at 500 °C for 10 h prior to its impregnation with cobalt nitrate solution. Different loadings of Re and Ru promoters were also added by incipient wetness impregnation of aqueous solutions of perhenic acid and ruthenium (III) nitrosylnitrate, respectively. A cobalt catalyst without promoter was used for comparison purposes. After the impregnation, all catalysts were dried at 120 °C and calcined at 450 °C for 3 h with a heating rate of 1 °C/min. The cobalt and promoters loadings were verified by an inductively coupled plasma (ICP) AES system. The designation and composition of the catalysts are listed in Table 1.

X-ray diffraction

XRD measurements were conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu/K$_\alpha$ radiation. Using Scherrer equation, the average size of the Co_3O_4 crystallites in the calcined catalysts was estimated from the line broading of a Co_3O_4 at 2θ of 36.8 degree.

Table 1: The designation and composition of the catalysts used in this study.

Catalyst	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
wt %	—	0.35%	0.7%	1.4%	2.0%	0.5%	1.0%	1.5%	2.0%
Promoter		Re	Re	Re	Re	Ru	Ru	Ru	Ru

Temperature programmed reduction

Temperature programmed reduction (TPR) profiles of the calcined catalysts were recorded using a Micromeritics TPD-TPR 290 system, equipped with a thermal conductivity detector. The catalyst samples were first purged in a flow of argon at 573 K, to remove traces of water, and then cooled to 313 K. The TPR of 50 mg of each sample was performed using 5.1 % hydrogen in argon gas mixture with a flow rate of 40 cm^3/min. The samples were heated from 313 to 1173 K with a heating rate of 10 K/min.

Hydrogen chemisorption and oxidation

The amount of chemisorbed hydrogen was measured using the Micromeritics TPD-TPR 290 system. 0.25 g of the calcined catalyst was reduced under hydrogen flow at 673 K for 12 h and then cooled to 373 K under hydrogen flow. The flow of hydrogen was switched to argon at the same temperature, which lasted about 30 minutes in order to remove the weakly adsorbed hydrogen. Afterwards the temperature programmed desorption (TPD) of the samples was obtained by increasing the temperature of the samples, with a ramp rate of 10 K/min, to 673 K under the argon flow. The TPD spectrum was used to determine the cobalt dispersion and its surface average crystallite size. After the TPD of hydrogen, the sample was reoxidized at 673 K by pulses of 10 % oxygen in helium to determine the extent of reduction. It is assumed that Co^o is oxidized to Co_3O_4.

BET surface area

BET specific surface area of the catalysts was measured by an ASAP-2000 system from Micromeritics. The catalyst samples were degassed at 473 K for 4 h under 50 mTorr vacuum and their BET area were determined using nitrogen adsorbent.

Fischer-Tropsch synthesis tests

The catalysts were evaluated in terms of their Fischer-Tropsch synthesis (FTS) activity (g HC produced/ g cat/ min) and selectivity (The percentage of the converted CO that appears as a given product) in a tubular fixed-bed micro-reactor. Typically, 0.5 g of the catalyst was charged into a 1/4" stainless steel tube, as the reactor. The reactor was placed in a molten salt bath with a stirrer to ensure a uniform temperature along the catalyst bed. The temperature of the bath was controlled via a PID temperature controller. Separate Brooks 5850 mass flow controllers were used to add H_2 and CO at the desired rate to a mixing vessel that was preceded by a lead oxide-alumina containing vessel to remove carbonyls before entering to the reactor. Prior to the activity tests, the catalysts were reduced in a flow of H_2 at 400 ^{o}C for 12 h. The temperature was raised to 400 ^{o}C with a heating rate of 1 K/min. The FTS tests were carried out at 210 ^{o}C, 1 atm, and a H_2/CO ratio of 2. The effluents of the reactor were analyzed for CO, CO_2, and C_1-C_{20} hydrocarbons, using an on-line Varian 3800 gas chromatograph. CO conversion and different product selectivity were calculated based on the GC analyses. Anderson-Schultz-Flory (A-S-F) distribution line was plotted for C_4^+ products to determine the chain growth probability, α.

RESULTS AND DISCUSSION

XRD patterns for the calcined Co/Al_2O_3 catalyst and those promoted by Re and Ru are shown in Figs. 1 and 2, respectively. The peaks at 46.1 and 66.5^o correspond to γ-alumina, while the other peaks, except the 49° peak, which is attributed to the cobalt aluminumate [15,16], relate to the different crystal planes of Co_3O_4. The cobalt aluminate peak is only distinguishable for the Co/Al_2O_3 catalyst. Both Figs. 1 and 2 show that the addition of Re and Ru promoters result in disappearance of the cobalt aluminate peak from XRD spectrum of the Co/Al_2O_3 catalyst. It seems that the promoters hinder the formation of cobalt aluminate in the calcination process. Also the average particle size of Co_3O_4 of different catalysts was calculated from broadening of the peak at $2\theta = 36.8^o$
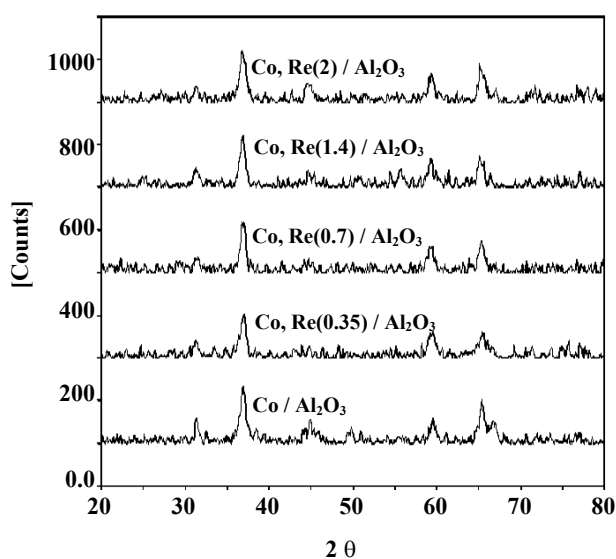
Fig. 1: XRD patterns of Co/Al₂O₃ (C₀) catalyst and those promoted by 0.35 to 2.0 % Re (C₁-C₄). The catalysts are calcined at 500 °C.

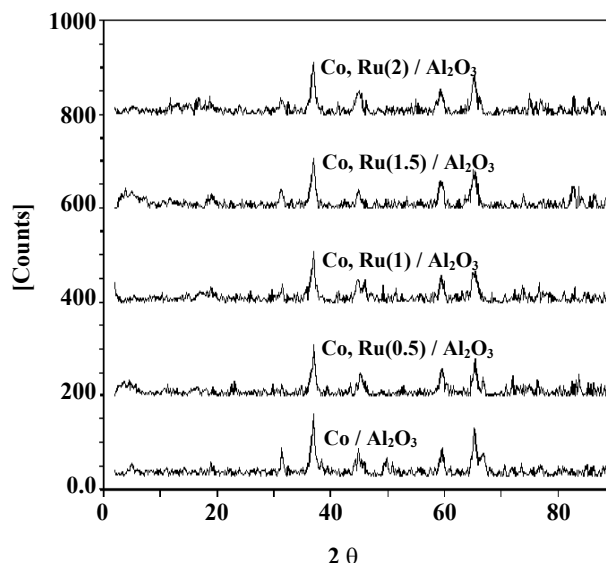***Fig. 2: XRD patterns of Co/Al₂O₃ (C₀) catalyst and those promoted by 0.5 to 2.0 % Ru (C₅-C₈). The catalysts are calcined at 500 °C.***

based on the Scherrer formula. Table 2 shows the average Co_3O_4 particle size of different catalysts. It demonstrates that, when Re and Ru are added to the cobalt catalyst, the average particle size is reduced.

Figs. 3 and 4 present the TPR spectra for the catalysts. The first peak is typically assigned to the reduction of Co_3O_4 to CoO, although a fraction of the peak likely comprise the reduction of the larger bulk-like CoO species to Co^o. The second broader peak, with a shoulder in some TPR spectra, is mainly assigned to the second step reduction, which is mainly reduction of CoO to Co^o. It also includes the reduction of cobalt species that interact with the support [17-19], which extends the TPR spectra to higher temperatures, such as the broad peak for Co/Al₂O₃ catalyst at about 640 °C. With addition of Re and Ru to the Co/Al₂O₃ catalyst the high temperature peak shifts to lower temperatures and also causes its tailing to get shorter. This indicates that the promoters reduce the extent of interaction of cobalt with alumina, which depends on the amount of promoter and the Co crystallite sizes, as is obtained from XRD spectra and indicated in Table 2.

Figs. 3 and 4 and Table 2 show that the addition of small amounts of Ru to the cobalt catalyst shifts both TPR peaks significantly to the lower temperatures. Addition of 0.5 wt.% Ru to the Co/Al₂O₃ results in a decrease in the temperature of the first TPR peak (FRT)
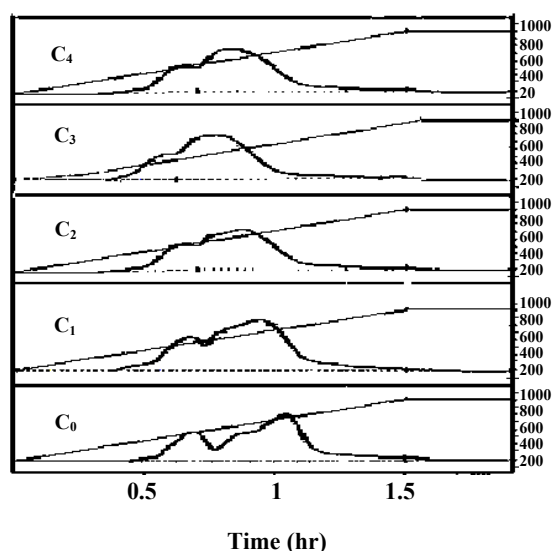
from 440 to 382 °C and the temperature of the second TPR peak (SRT) from 640 to 629 °C. Table 2 also shows the reducibility ratio for the whole TPR profile and that of the 1st and 2nd peaks, defined by the ratio of the areas of the corresponding peaks to that for Co catalyst. This is proportional to the amount of hydrogen consumed. The addition of 0.5 wt.% Ru to the cobalt catalyst, results in a significant improvement in the reducibility of the catalyst (Table 2). Increasing the Ru loading to 1.0 wt.% only resulted in a marginal effect in FRT and SRT and the catalyst reducibility. Further addition of Ru, decreases the reducibility to some extent. The Ru also enhances the reducibility of both Co_3O_4 and other Co oxide species, as indicated by the reducibility ratios and those of the 1st and 2nd peaks (Table 2). The 1st peak reducibility ratio is enhanced more than the 2nd one.

Das et al. have been showed that the reduction of ruthenium oxide occurs at temperatures lower than that of the cobalt. They have presumed that reduced Ru enhances the reduction of cobalt oxides, by spillover of hydrogen from Ru to the cobalt oxide. It may also enhance the reduction of smaller cobalt species that strongly interacts with the alumina support [13].
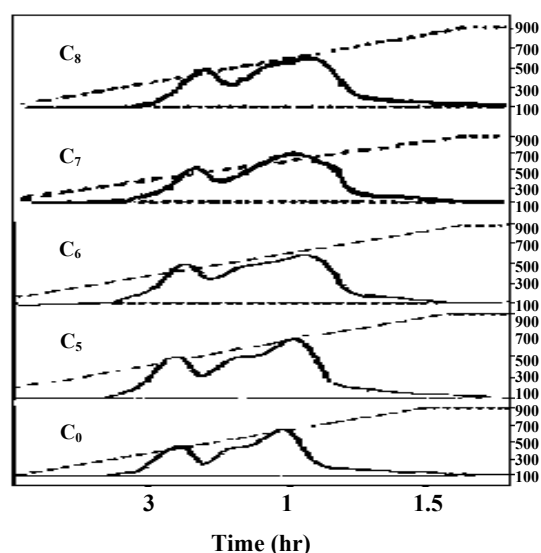
The same behavior for the enhancement of reducibility is observed for Re promoter. However, Re has no significant effect on the first TPR peak, as indicated in Table 2 by the 1st peak reducibility ratio, which is in

Table 2: Catalysts characterization data.

Catalyst Name	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
BET Specific Area (m^2/g)	165	164	155	153	152	155	154	153	151
XRD d_{Co3O4} (nm)	16.4	15.2	15	15	15.4	14.4	14.4	13.8	13.8
First TPR peak temperature (^{o}C)	440	437	437	435	435	382	378	372	371
Second TPR peak temperature (^{o}C)	640	595	525	510	511	629	624	620	620
1st Peak reducibility ratio	1.00	1.07	1.06	0.98	0.99	1.17	1.32	1.30	1.29
2nd Peak reducibility ratio	1.00	1.21	1.26	1.31	1.26	1.16	1.22	1.21	1.20
Reducibility ratio of TPR	1.00	1.17	1.19	1.27	1.22	1.16	1.25	1.22	1.22

Fig. 3: TPR patterns of Co/Al$_2$O$_3$ (C$_0$) catalyst from 40-1073 K and those promoted by 0.35 to 2.0 % Re (C$_1$-C$_4$).

Fig. 4: TPR patterns of Co/Al$_2$O$_3$ (C$_0$) catalyst from 40-1073 K and those promoted by 0.5 to 2.0 % Ru (C$_5$-C$_8$).

contrast with the effect of Ru on the reducibility of Co$_3$O$_4$ in the 1st peak. It still plays a significant role on decreasing the temperature of the second TPR peak (from 640 to 510 ^{o}C) for the reduction of Co species with significant interaction with the support. Rhenium oxide reduces at 350 ^{o}C, which explains the lack of its effect on the 1st low temperature peak [18,19]. The reducibility of the cobalt increases with the addition of Re, passes through a maximum at 1.4 wt.% Re and decreases

afterward (Table 2). Of particular importance, are peaks attributed to the reduction of Co species interacted with alumina at lower temperatures, which make more cobalt atoms to be available for FTS reaction.

The results of hydrogen temperature programmed desorption (TPD) and oxygen titration of the catalyst samples are given in Table 3. For each sample, uncorrected dispersion and particle size are calculated based on the total amount of cobalt in the catalyst samples.

Table 3: H₂ temperature programmed desorption and pulse reoxidation for Co/Al₂O₃ catalysts unpromoted and promoted with different amounts of Re and Ru promoters. The catalysts are calcined at 450 °C for 3h and reduced in hydrogen at 400 °C for 12 h.

Catalyst	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
μ mole H_2 desorbed /g cat.	79	147	155	170	158	134	163	143	142
μ mole O_2 Consumed /g cat.	595	972	1076	1201	1082	985	1154	1035	998
%Reduction	35	57	63	70.6	64	58	68.8	61.5	59.2
%Dispersion (Total Co)	6.2	11.5	12.2	13.3	12.4	10.6	12.8	11.3	11.1
%Dispersion (Reduced Co)	17.7	20.2	19.3	18.9	19.4	18.2	18.6	18.3	18.8
d_p(nm) (Total Co)	16.8	9.03	8.52	7.81	8.37	9.8	8.11	9.2	9.35
d_p(nm) (Reduced Co)	5.9	5.2	5.4	5.5	5.4	5.7	5.6	5.7	5.5

The percentage of reduction was measured from the oxygen titration after TPD, assuming Co^o is reoxidized to Co_3O_4. The calculated dispersion is corrected by the percentage reduction as follows:

$$\%D_{Total\ Co} = \frac{Number\ of\ Co^0\ atoms\ on\ surface}{Total\ number\ of\ Co\ atoms} \times 100$$

$$\%D_{Reduced\ Co} = \frac{Number\ of\ Co^0\ atoms\ on\ surface}{\left(Total\ number\ of\ Co\ atoms\right)} \times \frac{1}{\left(Fraction\ reduced\right)} \times 100$$

Table 3 shows that the hydrogen uptake increases up to two fold, with addition of ruthenium and rhenium to the Co/Al₂O₃ catalyst. The percentage reduction shows a remarkable increase when small amounts of Re or Ru are added to the Co/Al₂O₃ catalyst. The percentage reduction increases with the amount of Re added up to 1.4 % then decreases. The same behavior is observed for Ru promoted catalysts, for which the maximum occurs at about 1.0 %. Table 3 also shows that, by promoting the Co/Al₂O₃ catalyst with Re and Ru, while the dispersion of the cobalt crystallites calculated based on the total amount of cobalt increases significantly, the dispersion calculated based on the reduced cobalt does not change that considerably. The same results are observed for the decreasing of the Co particle sizes. These may be due to the reduction of smaller cobalt crystallites when the catalysts are promoted by Re or Ru. These crystallites have higher interaction with alumina as the support.

Figs. 5 and 6 represent the results of CO conversion, hydrogen uptake, and percentage reduction of cobalt for Co/Al₂O₃ promoted with different amounts of Re and Ru, respectively. Fig. 5 reveals that the addition of 0.35 % Re to the Co/Al₂O₃ dramatically enhances the CO conversion. Further addition of the Re up to 1.4 %, have less effect and extra Re addition causes the CO conversion to decrease slightly. Fig. 5 also shows that the trend for the CO conversion is similar to that for the hydrogen uptake and reduction percent. Fig. 6 reveals that the CO conversion increases, again in accordance with the reduction percent and hydrogen uptake, with addition of Ru to up to 1.0 %, and then slightly decreases. Figs. 5 and 6 reveals that the Fischer-Tropsch activity is strongly dependent on the surface reduced cobalt sites.

Fig. 7 shows the effect of Re and Ru on the selectivity of Fischer-Trposch synthesis to CH_4 and C_5^+ products. It clearly shows that, in addition to the significant enhancement of the CO conversion (Figs. 5 and 6), the methane selectivity reduces and that of C_5^+ increases by promoting the catalysts with Re and Ru. However, the effect of Re is less pronounced than Ru; C_5^+ selectivity is improved by 9.3 % for 0.7% Re, while that for 2 % Ru is enhanced by 23.1 %. At the same time the
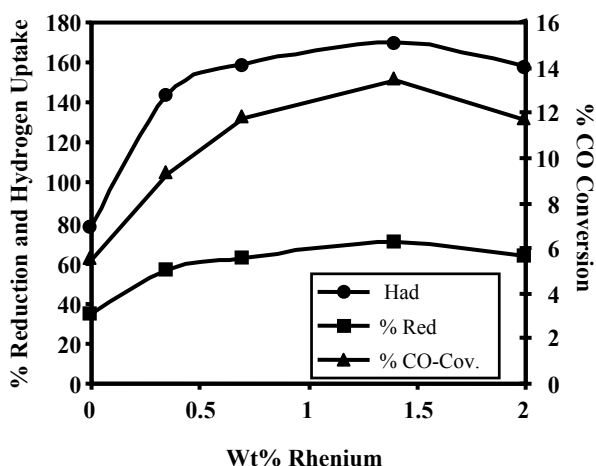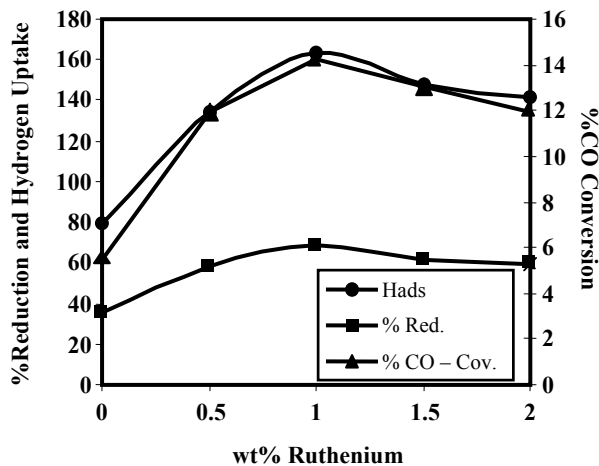
Fig. 5: Variation of CO conversion, percentage reduction, and hydrogen uptake with wt% of Re added to the Co/Al₂O₃ catalyst reduced at 400 °C for 12 h. Fischer-Tropsch synthesis is performed at 210 °C, 1 bar and H₂ / CO ratio of 2.

Fig. 6: Variation of CO conversion, percentage reduction, and hydrogen uptake with wt% of Ru added to the Co/Al₂O₃ catalyst reduced at 400 °C for 12 h. Fischer-Tropsch synthesis is performed at 210 °C, 1 bar at H₂ / CO ratio of 2.
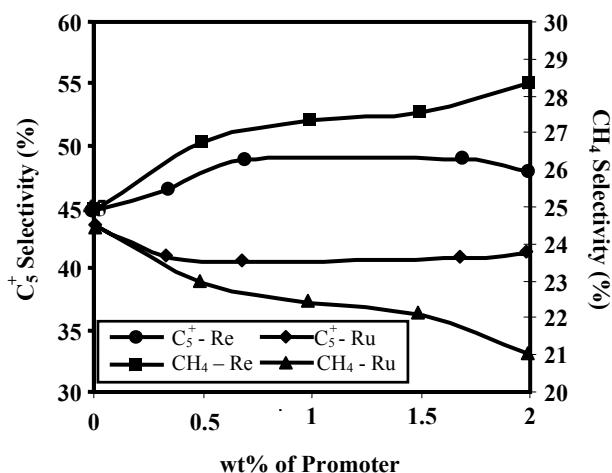

Fig. 7: Variation of methane and C_5^+ selectivity with different amounts of Re and Ru added to the Co/Al₂O₃ catalyst reduced at 400 °C for 12 h. Fischer-Tropsch synthesis is performed at 210 °C, 1 bar at H₂ / CO ratio of 2.
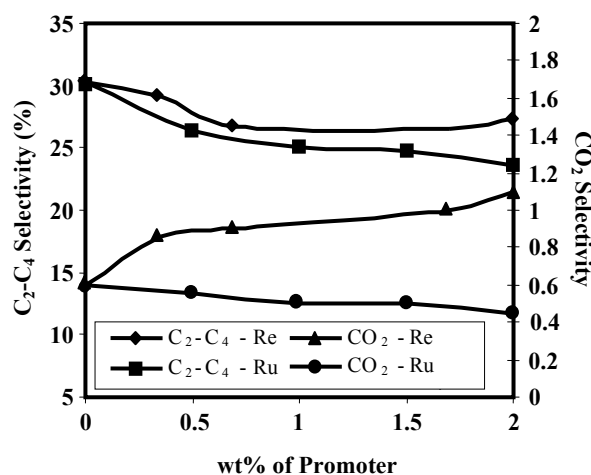

Fig. 8: Variation of CO_2 and C_2-C_4 selectivity of FTS with Re and Ru percentage of cobalt in the Co/Al₂O₃ catalyst reduced at 400 °C for 12 h.

0.7 % Re and 2 % Ru promoted catalysts, show 4 % and 14.3 % lower selectivity to methane, respectively. Addition of Re more than 0.7 % has slightly increased the selectivity to methane, whereas the selectivity to C_5^+ is diminished. This is in contrast to the effect of Ru; the selectivity to higher molecular weight FTS products monotonically increases with the amounts of Ru added to the catalyst.

The effect of the promoters on CO_2 and C_2-C_4 selec-

tivity are shown in Fig. 8. C_2-C_4 selectivity decreases by addition of both Re and Ru to the cobalt catalyst; the Ru is slightly more effective. The selectivity to CO_2 for Ru-promoted catalyst does not change significantly, whereas that for Re-promoted is almost doubled. As the amount of Re increases, CO_2 selectivity also increases. This may be attributed to the tendency of Re for CO adsorption [14] which presumably participate in the water-gas shift reaction which leads to the production of CO_2. It has been
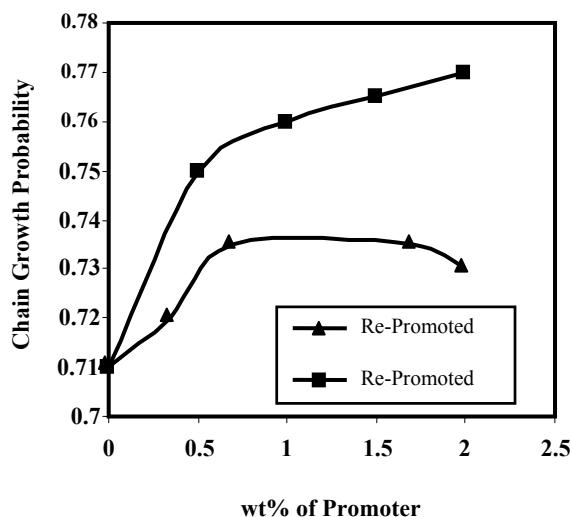
Fig. 9: Variation of chain growth probability (α) with different amounts of Re and Ru added to the Co/Al₂O₃ catalyst.

Fig. 10: Variation of CO conversion with wt% of Re and Ru added to the Co/Al₂O₃ catalyst.

reported that when Re alone is used as a catalyst in Fischer-Tropsch synthesis, about half of the products is CO_2 [3].

Chain growth probability (α) of FTS on different Re and Ru promoted cobalt catalysts is presented in Fig. 9. The α sharply increases when 0.5 % Ru is added to the cobalt catalyst, then it raises slowly with the amount of Ru in Co/Al₂O₃ catalyst. Ru is the most selective FTS catalysts towards higher molecular weight hydrocarbons. For 0.7 % Re-promoted cobalt catalyst the α increases from 0.71 to 0.74, then levels off.

It is believed that addition of Ru and Re promoters to the cobalt catalysts changes the catalyst morphology differently [20]. In the case of Ru promoter it has been reported that Ru mostly is enriched on the surface [8]. Whereas Re causes cobalt to enrich on the cobalt-rhenium alloy surface in their metallic states [14].

Fig. 10 compares the activity enhancement of cobalt catalyst upon promotion with Ru and Re. As is seen Ru-promoted catalyst improves the activity better than that of Re-promoted catalyst. This improvement cannot be only attributed to the extent of reducibility, which improves with both promoters. If this was the case, the activity improvement of Re promoted catalyst should have been even better compared to the Ru-promoted catalyst. Therefore, it seems that there should be another parameter other than the extent of reducibility, which affects the activity improvement. Considering the higher activity of
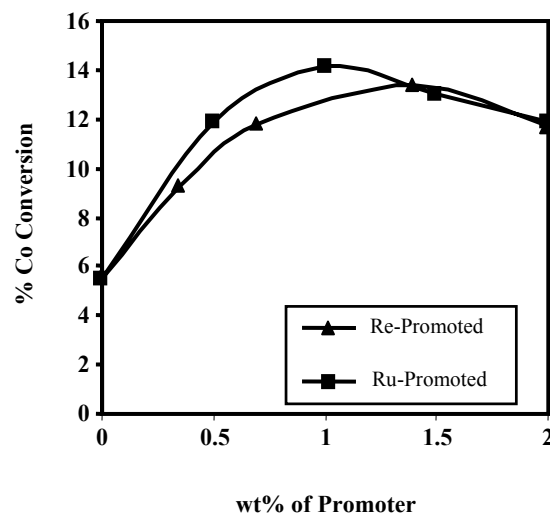
Ru with respect to cobalt and its enrichment on cobalt surface as opposed to Re may be another cause for the better activity improvement in Ru promoted catalyst.

Average turn over frequency calculated for un-promoted, Re-promoted and Ru-promoted catalysts are: 0.658×10^{-2}, 0.675×10^{-2} and 0.7735×10^{-2} (mole CO converted/g-atom Co-s) respectively. *Iglesia* [7] reported the TOF for cobalt catalyst supported on Al₂O₃, SiO₂, TiO₂, and MgCr₂O₄ is in the range of $1.6 \times 10^{-2} - 3.0 \times 10^{-2}$. The difference is attributed to the difference in pressure. The pressure in this work is atmospheric, whereas the pressure used by *Iglesia* is about 20 atm.

These turnover rates supports the discussion made in the above paragraph, i.e., Ru improves the catalyst activity better than the Re. These rates also support the suggestion that Ru improvements are not only the result of improvement in the cobalt reduction.

Comparing the turnover rates for unpromoted and Re-promoted catalysts, which are close enough, it may be concluded that Re does not change the intrinsic activity of the active sites. Whereas, Ru improvements is not restricted to the improvements in reducibility of the cobalt catalyst.

Ru also is more selective towards higher molecular weight hydrocarbons than cobalt. Therefore the more improvement in C_5^+ selectivity observed (Fig. 7) for Ru promoted catalysts as compared to Re promoter may be due to the Ru enrichment on the cobalt crystallite surface.

CONCLUSION

The effects of Ru and Re as promoters for Co/Al_2O_3 Fischer-Tropsch catalysts were investigated. Both promoters enhance the reducibility of the Co. The Re enhances the reducibility of the CoO to Co^0 and small cobalt oxide particles with higher interaction with the support. In addition to enhancing the reducibility of CoO to Co^o and small cobalt oxide species, which interact with the support, Ru improves the reducibility of Co_3O_4 to CoO. A small amount of the promoters increases the number of cobalt active sites, which results in a dramatic enhancement of the CO conversion activity. 1 wt % Ru and 1.4 wt % Re increased the activity of the catalyst by a factor of 2.8 and 2.5 respectively. Both promoters enhance the selectivity of Fischer-Tropsch synthesis towards the higher molecular weight hydrocarbons. However, this enhancement is more pronounced for Ru and increases monotonically with the percentage of Ru added, while that for Re is limited to 0.7 %. As opposed to Ru, Re increases the CO_2 selectivity, even as compared to unpromoted Co/Al_2O_3 catalyst. Investigations on the effect of the promoters on the deactivation rate of the catalysts at higher conversions and the effect of water is underway.

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