

Accelerated Deactivation and Activity Recovery Studies of Ruthenium and Rhenium Promoted Cobalt Catalysts in Fischer-Tropsch Synthesis

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ABSTRACT: Accelerated deactivation of Co/Al₂O₃ catalysts in Fischer-Tropsch synthesis and the effect of Re and Ru as the catalytic promoters are reported. 15wt% Co/Al₂O₃ catalyst and 1wt% Ru and 1.4wt% Re promoted cobalt catalysts have been formulated and extensively characterized. The deactivation of the unpromoted cobalt catalyst and those promoted with Re and Ru were studied by accelerated method at 260°C. Different sources of deactivation were identified. The amount of activity recovery after regeneration at the conditions of low temperature treatment at 260°C and high temperature treatment at 400°C for the used promoted and unpromoted catalysts were determined. It was revealed that promoted catalyst deactivated faster than unpromoted ones. High temperature H₂ treatment restored the catalytic activity of the catalysts more than 97.5%.

KEY WORDS: Fischer-Tropsch, Cobalt, Ruthenium, Rhenium, Deactivation, Activity Recovery.

INTRODUCTION

Interest in the Fischer-Tropsch synthesis (FTS) for hydrocarbon production from natural gas is increasing in viewpoint of clean fuel production. One of the major elements in FT synthesis is the catalyst being used. A good FTS catalyst has three major characteristics: high activity, high selectivity towards liquid products and most importantly long lifetime. Among the catalysts used for this synthesis are cobalt and iron based catalyst. Due to low water gas shift activity and high chain growth probability, cobalt containing catalysts are among the

best candidates for Fischer-Tropsch synthesis. Cobalt catalysts are more expensive than Iron catalysts and therefore, lowering the deactivation rates of them are one of the main challenges facing the commercial development of these catalysts. Thus, several research groups recently have investigated the deactivation rates of these catalysts [1-9]. *Hilmen et al.* [2] have shown that Al₂O₃-supported cobalt catalysts, and especially those with promoters such as Re, which are suitable for improving the reducibility of the catalysts, deactivate

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faster. They attributed this effect to higher reaction rates which in turn increases the partial pressure of water which is known to be one of the major sources for deactivation. *Li, et al.* [8] by changing P_{H_2O}/P_{CO} ratios, by cofeeding of water and changing the space velocity of the reactants, observed a decrease in CO conversion.

They found that at low P_{H_2O}/P_{CO} ratios, the extent of deactivation was low and reversible. However, at higher ratios deactivation was high and permanent. *Kiss, et al.* [6] studied hydrothermal deactivation of silica supported cobalt catalysts. They demonstrated that high partial pressure of water resulted in formation of a phase containing mixed oxides of support and cobalt which is inactive for the synthesis. Low-temperature hydrogen treatment did not recover cobalt from this mixed oxide phase but high-temperature reduction in flowing H_2 restored the catalytic activity. *Krishnamoorthy, et al.* [7] have shown that when water was added to the Co-catalyzed FTS, the selectivity to olefins and C_5^+ products were enhanced. Water presence in the pores causes CO to be solved more than hydrogen which in turn lowers the termination rates of surface alkyl chains and increases C_5^+ selectivity.

Das, et al. [1] by EXAFS studies have shown that sintering process is the major source of the deactivation of the cobalt catalysts.

In our previous work we showed that Ru and Re could improve the reducibility, catalytic activity and C_5^+ hydrocarbon selectivity of Fischer-Tropsch synthesis. 1wt% Ru and 1.4wt% Re increased the activity of the catalyst by a factor of 2.8 and 2.65 respectively [10]. Both promoters enhanced the selectivity of Fischer-Tropsch synthesis towards the higher molecular weight hydrocarbons. In the present work, the deactivation of unpromoted 15wt% Co/ Al_2O_3 catalyst and 1wt% Ru and 1.4wt% Re promoted catalysts have been investigated. The nature of deactivation of the catalysts were studied by accelerated method, and different sources of deactivation were identified. The deactivated catalysts were treated under hydrogen flow to restore the activity. The hydrogen treatment were performed at two different temperatures i.e. 260 and 400°C. Both fresh and used catalysts were extensively characterized by different methods, including elemental analysis, BET physisorption, particle size distribution, X-ray diffraction, hydrogen chemisorption, and temperature programmed reduction.

EXPERIMENTAL

Catalyst preparation

The 15 wt% Co/ γ - Al_2O_3 catalyst was prepared by incipient wetness impregnation of alumina with a specific surface area of 200 m^2/g . The support was calcined at 500°C for 10 h prior to its impregnation with cobalt nitrate solution. Catalysts with 1.4% of Re and 1% of Ru promoters were also prepared by incipient wetness impregnation of aqueous solutions of perhenic acid and ruthenium (III) nitrosyl nitrate, respectively. After the impregnation, all catalysts were dried at 120°C and calcined at 500°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.

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 broadening of a Co_3O_4 at 2θ of 36.8°.

Temperature programmed reduction

Temperature programmed reduction (TPR) spectra of the 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 spectra of 50 mg of each sample was obtained using 5.1% hydrogen in argon gas mixture with a flow rate of 40 cm^3/min . The samples were heated from 313 to 1273 K with a heating rate of 10 K/min. Measurements were done before and after reaction. The used catalyst were reoxidized with a gas containing 1% O_2 after the reaction and before TPR tests.

Hydrogen chemisorption and oxidation

The amount of chemisorbed hydrogen was measured using the Micromeritics TPD-TPR 290 system. 0.25 g of the calcined catalysts were 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^0 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.

Reaction testing

A series of experiments were designed to study the accelerated deactivation of the cobalt catalysts and its effects on the product distribution of FTS. 1.5 gr of the catalysts was charged in a 1/4" tubular fixed-bed micro-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 metal carbonyls before entering to the reactor. Fig. 1 shows the experimental setup. Prior to the activity tests, the temperature was raised to 400°C with a heating rate of 1 K/min and the catalysts were reduced in a flow of H_2 at 400°C for 12 h (first treatment step). The FT synthesis (first synthesis step) was carried out at 260°C, a total pressure of 1 bar, and a H_2/CO ratio of 2. Also a low feed flow rate of 30 mL/min was used to achieve high conversions and high water partial pressures that further accelerate the deactivation of the catalyst. Analyses of CO, CO_2 , and $\text{C}_1\text{-C}_{15}$ hydrocarbons, were performed in an on-line modified refinery gas analyzer (Varian 3800) every one-hour and CO conversion and selectivity (the percentage of the converted CO that appears as a given product) of the products were calculated. After 48 h of the first FT synthesis step, the flow of CO was switched off and catalyst was treated (second treatment step) in a flow rate of 120 mL/min H_2 at 260°C for 4 h. Then the

second FT synthesis step was carried out at the same conditions of the first synthesis step and the activity (g HC produced/ g cat/ min) and selectivity of the catalyst were measured. The third treatment step of the catalysts was performed at 400°C for 6 h. Subsequently the catalyst was cooled to 260°C and the third FT synthesis step was carried out at the same conditions of the previous synthesis steps.

Measurement of coke deposition

The amount of coke deposition on the catalysts was measured by UOP 703 standard method [11] after the third FT synthesis step. The samples were pretreated for the coke measurements as follows:

After the third FT synthesis step, the samples were treated under hydrogen flow of 120 mL/min starting from 260°C and by a ramp rate of 10 K/min raised to 400°C. The exit flow was monitored for CH_4 until its concentration was null.

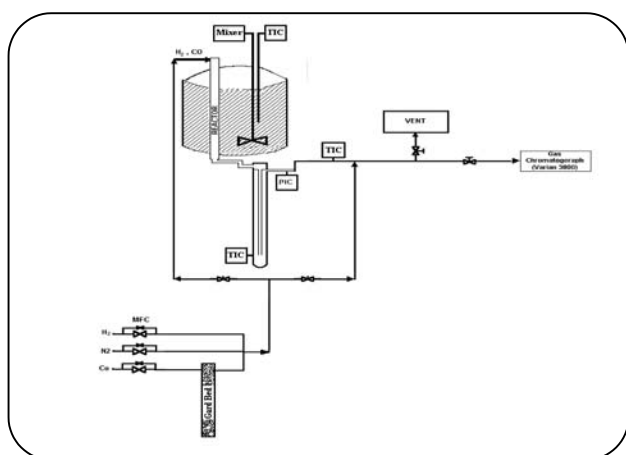
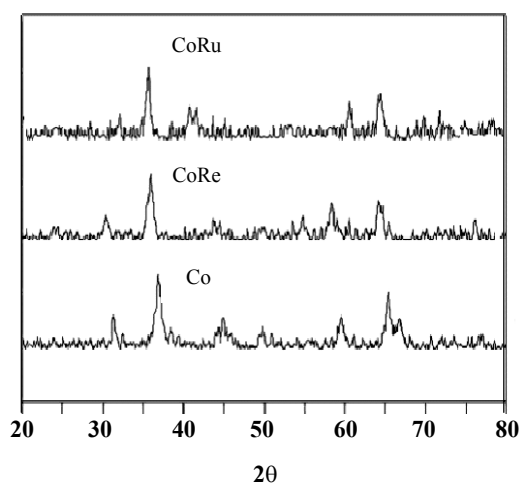
RESULTS AND DISCUSSION

XRD patterns for the calcined $\text{Co}/\text{Al}_2\text{O}_3$ catalyst and the ones promoted by 1.4 wt% Re and 1.0 wt% Ru are shown in Fig. 2. The peaks at 46.1 and 66.5° correspond to γ -alumina, while the other peaks, except the 49° peak which is attributed to the cobalt aluminate [5,12], relate to the different crystal planes of Co_3O_4 . The cobalt aluminate peak is only distinguishable for the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst. Fig. 2 shows that the addition of Re and Ru promoters to the $\text{Co}/\text{Al}_2\text{O}_3$ result in disappearance of the cobalt aluminate peak from XRD spectrum. It seems that the promoters suppress the formation of cobalt aluminate in the calcination process. Also the average particle size of Co_3O_4 of different catalysts were calculated from broadening of 36.8° peak and the Scherrer formula. Table 1 displays 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.

XRD patterns of used catalysts are shown in Fig. 3. The resulting spectra are very complex. Support peaks for all the samples appear at 46.1 and 66.5°. Peaks for cobalt metal are appeared at 2θ values of 44.2, 51.5 and 75.2° for Co catalyst and 2θ values of 44.2, 51.5 and 75° for CoRe catalyst and 2θ values of 43.8, 51.5 and 75.6° for CoRu catalyst in the spectra. These peaks correlate with the reported literature values for a cubic cobalt structure

Table 1: Characterization data of the calcined and used catalysts.

Catalyst Name	15wt% Co/Al ₂ O ₃	1.4%Re 15wt% Co/Al ₂ O ₃	1.0%Ru 15wt% Co/Al ₂ O ₃
BET Specific Area (m ² /g)	165	153	154
XRD d _{Co₃O₄} (nm)	16.4	15	14.4
1 st TPR peak temperature (K), (calcined)	684	685	651
2 nd TPR peak temperature (K), (calcined)	913	816	875
3 rd TPR peak temperature (K), (calcined)	1073	-	-
1 st TPR peak temperature (K), (used)	670	659	604
2 nd TPR peak temperature (K), (used)	-	-	-
3 rd TPR peak temperature (K), (used)	1073	1074	1073
1 st TPR peak H ₂ consumption (μmol H ₂ /g) (calcined)	1004.7	998.2	1428.9
2 nd TPR peak H ₂ consumption (μmol H ₂ /g) (calcined)	3284.8	4262.6	3985.36
3 rd TPR peak H ₂ consumption (μmol H ₂ /g) (calcined)	78.9	-	-
1 st TPR peak H ₂ consumption (μmol H ₂ /g) (used)	3994.1	4322.6	4977.7
2 nd TPR peak H ₂ consumption (μmol H ₂ /g) (used)	-	-	-
3 rd TPR peak H ₂ consumption (μmol H ₂ /g) (used)	156.4	342.1	217.6

**Fig. 1: Experimental setup.****Fig. 2: XRD patterns of calcined catalysts.**

[5,13]. The peaks at 2θ values of 41.3 , 42.5 , 45.7 and 56.5° for Co catalyst and 2θ values of 42.5 , 45.7 and 71° for CoRe catalyst and 2θ values of 41.3 , 45.7 and 56.5° for CoRu catalyst in the spectra correlate well with Co_2C . Of particular importance the peaks at 2θ values of 29.6 , 49 and 78° which may correspond to CoAl_2O_4 spinel at the spectra's of Co, CoRe and CoRu catalysts [5]. Also the peaks at 2θ values of 36.5 , 42.5 , 60 and 62.5° at the spectra of Co and 36.5 , 42.5 , 60 and 62.5° at the spectra of CoRe and 36.5 , 42.5 and 60° at the spectra of CoRu can be attributed to the different crystal planes of cobalt oxides [5,13]. Several peaks were also observed at different 2θ values in the spectra of the catalysts but no assignment for these peaks could readily be ascertained.

These results suggest that during FT synthesis, different cobalt species are formed, some of which can be regenerated to cobalt during different hydrogen treatment steps. Although a fraction of cobalt clusters may oxidize in presence of significant amount of water formed during FT synthesis with high conversions, predominant amount of the cobalt oxide in the sample (Fig. 2) most probably is formed in the passivation step. Also it seems that a small amount of Co_2C is formed during the FT synthesis. The cobalt aluminate peaks appeared in the used promoted samples may have been formed during the FT synthesis. Significant amount of water formed in the FT synthesis helps the formation of the cobalt aluminate [1,3,4,5,8,13].

Figs. 4 and 5 present the TPR profiles of the calcined and reoxidized used catalysts. In the profile of the fresh 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^0 . The second broader peak, with a shoulder in unpromoted catalyst, is mainly assigned to the second step reduction, which is mainly reduction of CoO to Co^0 . It also includes the reduction of cobalt species that interact with the support [3,4,13], which extends the TPR spectra to higher temperatures, such as the broad peak for $\text{Co}/\text{Al}_2\text{O}_3$ catalyst at about 913 K. With addition of Re and Ru to the $\text{Co}/\text{Al}_2\text{O}_3$ 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 size, as was revealed from XRD spectra and indicated in Table 1.

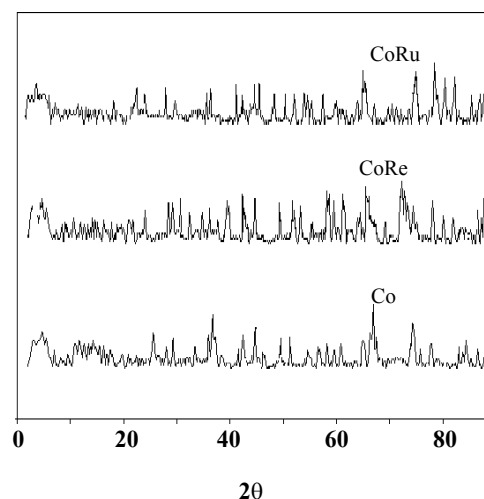


Fig. 3: XRD patterns of pasivated used catalysts. The synthesis was performed at 260°C , 1 bar at H_2/CO ratio of 2.

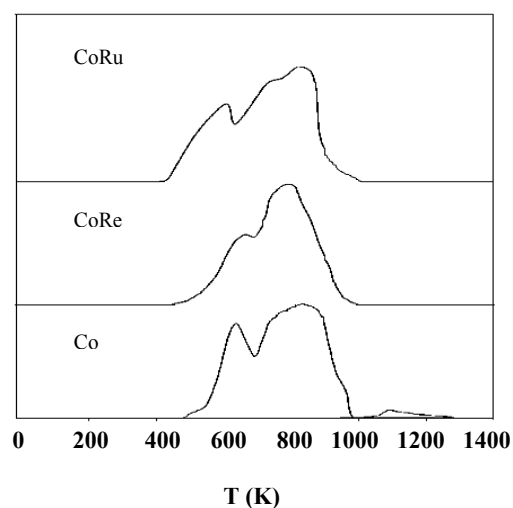


Fig. 4: TPR patterns of calcined catalysts from 40-1273 K.

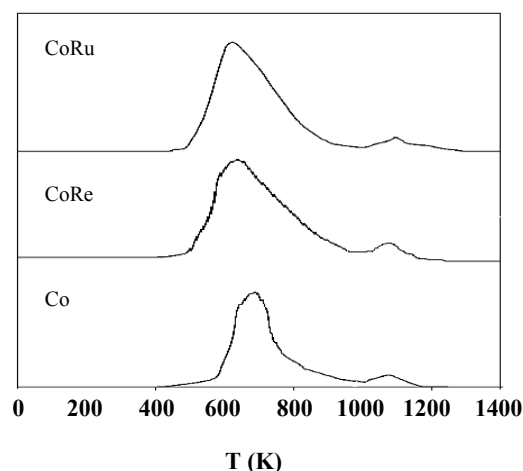


Fig. 5: Relative activity of catalysts with time on stream ($T=260^\circ\text{C}$, $P=1$ bar).

Fig. 4 and Table 1 show that the addition of Ru to the cobalt catalyst significantly shifts both TPR peaks to the lower temperatures. Addition of 1 wt.% Ru to the Co/Al₂O₃ results in a decrease in the temperature of the first TPR peak from 684 to 651 K and the temperature of the second peak from 913 to 875 K. Table 1 also shows the measured H₂ consumption for the calcined catalysts. This table demonstrates that the addition of 1 wt.% Ru to the cobalt catalyst, results in a significant improvement in the reducibility of the cobalt catalyst. The Ru also enhances the reducibility of both Co₃O₄ and other Co oxide species, as indicated by the measured H₂ consumption of the 1st and 2nd peaks. The 1st peak is enhanced more than the 2nd one. Das, et al. [1] have shown 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.

The Re promoter affects the reducibility of cobalt catalyst differently. Rhenium has no significant effect on the first TPR peak, as indicated in Table 1 by hydrogen consumption for the 1st peak. It still plays a significant role on lowering the temperature of the second TPR peak from 913 to 816 K. Rhenium oxide itself reduces at about 620 K, which explains the lack of its effect on the 1st low temperature peak [4,13]. Lowering the temperature of the second peak that is partly attributed to the reduction of Co species interacted with alumina make more cobalt metal to be available for FTS reaction.

CoAl₂O₄ can also be formed during calcination and may be reduced approximately at 1100 K. This phase is not observed in TPR of calcined Re and Ru promoted catalysts. However a very small peak at about 1080 K in TPR of the unpromoted catalyst may indicate the formation of cobalt aluminate during calcination process for this catalyst [2,14].

TPR of the used catalysts may be compared with those of fresh calcined catalysts to see the formation of different phases in the course of FT reaction. Fig. 5 demonstrates that the following changes has occurred due to the reaction:

1- The two peaks in TPR of the fresh calcined catalysts have been transferred to one peak at slightly lower

temperature with a broad tailing extended up to 900 K.

2- A peak at about 1073 K. This peak was present for the fresh calcined unpromoted catalyst. However its area was measured to be about twice of the fresh catalyst.

3- A peak at about 1073 K for the Ru and Re promoted catalysts. It should be noted that this peak is not observed in the TPR of the fresh catalysts.

Thus, it seems that during the reaction, the formation of cobalt aluminate phase is enhanced even for the promoted catalysts. The broad tailing of this peak in all catalysts to about 900 K was mainly assigned to the reduction of cobalt species that interact with the support, which extend the TPR spectra to higher temperatures [2,3,4,14]. This indicates that FT synthesis also in the presence of Re and Ru promoters increases the extent of interaction of cobalt with alumina.

Fig. 5 and Table 1 also show that in the presence of Ru and Re promoters, the reduction of the cobalt oxides of the used catalysts occur at lower temperatures as compared with the unpromoted catalyst. The hydrogen consumption for these catalysts follow the same trend indicating that the reducibility of the used promoted catalysts are quite better than the unpromoted ones.

However, the effect of Re with regard to these enhancement is lower than that of Ru. Also the area of the high temperature peak increased upon promotion of the catalyst with Re and Ru which reveals that the formation of cobalt aluminate is higher for the promoted catalysts than the unpromoted one during the reaction.

It has been shown for alumina-supported cobalt catalysts the presence of water shifts the TPR-peaks to higher temperatures and promotes the formation of Co-phases with reduction properties similar to cobalt aluminates [2,14]. Arnoldy and Moulijin [15] have studied the effect of calcination condition on Co/Al₂O₃ catalyst by TPR. They showed the changes in TPR profile with raising the calcination temperatures. The TPR profiles presented in Fig. 5 resemble the TPR of Co/Al₂O₃ catalysts calcined above 920 K [15]. They explained the effects by increasing of the diffusion of Co²⁺ (and Al³⁺) above this temperature which leads to formation of Co²⁺ with O-Al ligands or cobalt aluminate spinel, and also exchange of Co²⁺ in Co₃O₄ with Al³⁺. Although our experiments are done at lower temperatures, similar mechanism seem to be valid. It is possible that water produced during FTS increases the mobility of ions on

the support and therefore enhances Co-Al interaction. Enhancement in aluminate formation rates by Re and Ru promoted catalysts could be the result of higher partial pressure of water during the synthesis as a result of higher rate of FTS over these catalysts [2].

The results of hydrogen temperature programmed desorption (TPD) and oxygen titration of the catalyst samples are given in Table 2. For each sample, uncorrected dispersion and particle size are calculated based on the total amount of cobalt in the catalyst samples. The percentage of reduction was measured from the oxygen titration after TPD, assuming Co^0 is reoxidized to Co_3O_4 . The dispersion based on total number of cobalt atoms and total number of reduced cobalt atoms are calculated as follows:

$$\%D_{\text{Total Co}} = \frac{\text{No. Of Co}^0 \text{ Atoms on Surface}}{\text{Total No. Co Atoms}} \times 100$$

$$\%D_{\text{Reduced Co}} = \frac{\text{No. Of Co}^0 \text{ Atoms on Surface}}{(\text{Total No. Co Atoms}) \times (\text{Fraction Reduced})} \times 100$$

Table 2 shows that with addition of ruthenium and rhenium to the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst, the hydrogen uptake increases up to two fold. The percentage reduction shows a remarkable increase when Re or Ru are added to the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst. Table 2 also shows that, in the presence of Re and Ru promoters, while the dispersion of the cobalt crystallites based on the total number of cobalt increases significantly, the dispersion based on the reduced cobalt does not change 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 [10]. These crystallites have higher interaction with alumina as the support.

Table 3 represents the results of CO conversion, selectivity of Fischer-Tropsch synthesis to CH_4 , $\text{C}_2\text{-C}_4$, C_5^+ and CO_2 products for unpromoted and promoted catalysts at 210 and 260 °C. This table clearly demonstrates that, in addition to the significant enhancement of the CO conversion, the methane selectivity reduces and that of C_5^+ increases by promoting the catalysts with Re and Ru at 210 and 260 °C. However, the effect of Re is less pronounced.

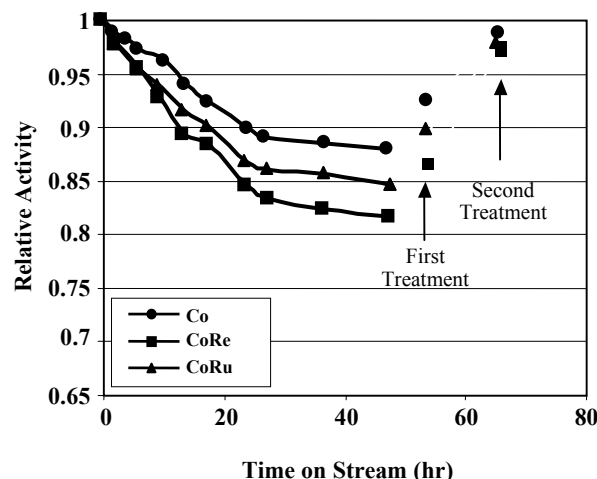


Fig. 6: Relative activity of catalysts with time on stream ($T = 260^\circ\text{C}$, $P = 1 \text{ bar}$).

Fig. 6 presents the relative activity changes with the duration of FT synthesis before and after different hydrogen treatment steps. Relative activity is defined as the CO conversion at a specified time to the initial CO conversion of the FT synthesis. The conditions and the reaction sequence for the synthesis were described in experimental section. As is observed during the 48 h FT synthesis the relative activity of the Co, CoRe, CoRu catalysts reduce upto about 25 h time on stream, then levels off. The relative activity changes are higher in order of the Re-promoted > Ru-promoted > unpromoted cobalt catalysts. For unpromoted catalyst, the relative activity declines by 8% in the 25 h while the activity fall for CoRe and CoRu are 16.8 and 14% respectively. After second hydrogen treatment step at 260°C the relative activities increases by 4.6, 5 and 5.4% for Co, CoRe and CoRu catalysts, respectively. This type of deactivation is a small fraction of total activity loss in Re and Ru promoted catalysts and is almost equal to deactivation of the unpromoted catalyst.

Finally after the third reduction step at 400°C, the relative activities increase by 3.7, 10.9 and 8.4% for Co, CoRe and CoRu catalysts, respectively.

There are different types of deactivation processes for the catalysts that can be partially recovered in the various hydrogen treatment steps. In the second hydrogen treatment step 4.6-5.4% of activity of different catalysts is reversed by mild reduction at 260°C. It has been suggested that in FT synthesis on alumina-supported

Table 2: H₂ temperature programmed desorption and pulse reoxidation for the calcined catalysts .**The catalysts were calcined at 500 °C for 3h and reduced in hydrogen at 400 °C for 12 h.**

Catalyst	15wt% Co/Al ₂ O ₃	1.4%Re 15wt%Co/Al ₂ O ₃	1.0%Ru 15wt%Co/Al ₂ O ₃
μ mole H ₂ desorbed /g cat.	79	170	163
μ mole O ₂ Consumed /g cat.	595	1201	1154
%Reduction	35	70.6	68.8
%Dispersion (Total Co)	6.2	13.3	12.8
%Dispersion (Reduced Co)	17.7	18.9	18.6
d _p (nm) (Total Co)	16.8	7.81	8.11
d _p (nm) (Reduced Co)	5.9	5.5	5.6

Table 3: Variation of CO conversion, CH₄, C₂-C₄, C₅₊ and CO₂ selectivity of the catalysts. The catalysts reduced at 400 °C for 12 h and Fischer-Tropsch synthesis was performed at 210 and 260 °C, 1 bar at H₂/CO ratio of 2.

Catalyst Sample	Temperature (°C)	CO Conversion (%)	CH ₄	C ₂ -C ₄	C ₅ ⁺	CO ₂
Co	210	5.50	24.50	30.20	44.70	0.60
	260	53	62.10	21.31	3.79	12.80
CoRe	210	13.40	23.60	26.50	48.90	1.00
	260	98.03	58.90	16.42	3.88	20.80
CoRu	210	14.20	22.40	25.10	52	0.50
	260	97.91	57.10	21.25	5.25	15.40

cobalt catalysts at high conversion, the loss in active sites is caused by water-induced oxidation of cobalt [7]. This water-induced back-oxidation of cobalt can be largely reversed and catalytic activity can be recovered by hydrogen treatment at or close to FT synthesis conditions. This deactivation process does not involve metal-support interactions but rather entail cobalt redox transformation with no support participation [7]. It is also proposed that bulk oxidation of large Co metal crystallites to CoO or Co₃O₄ is not thermodynamically favored at typical FT synthesis conditions, but metal-oxygen bonds at metal surfaces are stronger than in the bulk oxides, making the

oxidation of Co surfaces possible even when bulk oxidation is unfavorable [9,16].

In the third hydrogen treatment step at 400°C, the relative activities of all catalysts are recovered more than 97.5%. This recovery of the activities for CoRe and CoRu catalysts are about 2-3 times higher than that for the Co catalyst. This is due to higher rate of deactivation observed during the 48 h FT synthesis on the Re and Ru promoted catalysts, which is not recovered during the second mild hydrogen treatment step (see Fig. 6).

The larger recovery of deactivation observed for CoRe and CoRu catalysts seems to be caused by

regeneration of more refractory forms of oxidized cobalt generated by cobalt-alumina interactions [13]. The extent of this type of deactivation depends on the partial pressure of water produced during Fischer-Tropsch synthesis. It was suggested that water promotes interaction between cobalt oxide species and γ -Al₂O₃ support [13]. The result (Fig. 6) suggest that Re and Ru promoted catalysts are more susceptible to reoxidation and cobalt-alumina interactions than the unpromoted catalyst. Faster deactivation rate observed for the Re and Ru promoted catalysts in this type of deactivation can be likely attributed to two factors of water partial pressure and cobalt crystallites size distribution. The increased activity of Re and Ru promoted catalysts, due to more active sites, will yield a higher water partial pressure in the reactor that leads to higher rate of deactivation.

H₂ chemisorption and oxygen titration data (Table 2) show that smaller cobalt crystallites are formed on the Re and Ru promoted catalysts. The reduction of these crystallites in the first hydrogen treatment step is enhanced by the promoters. This leads to higher initial activity of the promoted catalysts as compared to the unpromoted one. However, the small metal clusters more strongly produced during the hydrogen treatment is calculated based on adding up the carbon constituents of all hydrocarbons detected. For the same hydrogen treatment, interact with alumina support during high conversion FT synthesis with high water partial pressure and tend to be more prone to oxidation than larger bulk like cobalt crystallites because of their extensive contact with oxide support [3,13]. Table 2 indicates that the small cobalt clusters may not be reduced in the unpromoted catalyst leading to lower initial activity of the catalyst and therefore lower deactivation rate and recovery in the final hydrogen treatment step at 400 °C.

Fig. 6 also present that the Re promoted catalyst shows higher rate of deactivation, as compared to the Ru-promoted one. In accordance with the above discussion, Table 2 shows that the Re promoted catalyst has lower cobalt crystallite sizes and higher percentage of reduction.

The percentages of relative activity that could not be recovered by hydrogen treatment at 400 °C (Fig. 6) are 1.2%, 2.5%, 2.3% for Co, CoRe and CoRu catalysts, respectively. Formation of some types of irreducible cobalt aluminates, sintering or cluster growth and finally

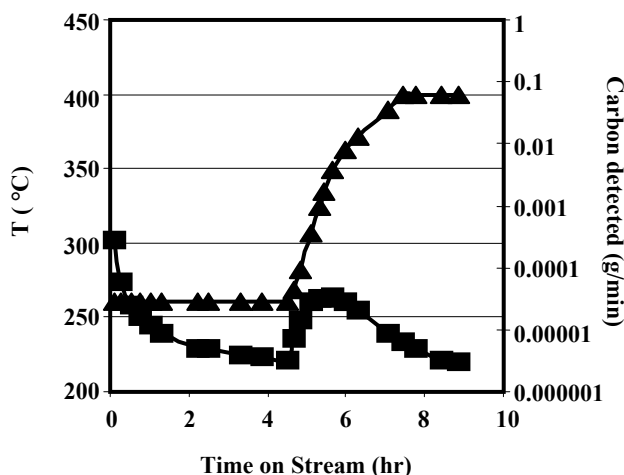


Fig. 7: Rate of carbon in the hydrocarbons produced during the hydrogen treatment of 1.4%Re promoted Co/Al₂O₃ catalyst with time on stream and treatment temperature.

refractory coke formation may be the source of this irreversible activity loss. The formation of irreducible cobalt aluminates was clearly identified by XRD and TPR spectra of the used Co, CoRe and CoRu catalysts as shown in Figs. 3 and 5, Jacobs, *et al.* [4] by EXAFS studies have shown that above 25% water addition, the sudden irreversible loss in activity is due to reaction of the cobalt clusters with the support, forming cobalt aluminates-like species. In addition, as compared to the unpromoted catalyst, there is a greater number of metal cluster on the same surface area of alumina in CoRe and CoRu catalysts and smaller metal clusters with a greater fraction of surface atoms. The small clusters are more unstable than the larger ones and more susceptible to sintering process that may lead to a faster sintering rate in these catalysts. In a similar work Das, *et al.* [4], by studying the alumina supported cobalt catalyst in the CSTR reactor, have shown that the average metal cluster size has increased with time on stream.

Fig. 7 shows the hydrogen treatment of carbonaceous materials, when synthesis gas (after 48 h FT synthesis at 260 °C) is switched to hydrogen. The reactor was kept at 260 °C for 4.5 h, then the temperature was raised to 400 °C and kept there for 1.5 h. The rate of carbon in the hydrocarbons the selectivity to different hydrocarbons is presented in Fig. 8.

Figs. 7 and 8 show a rapid decay in the rate of carbon content of hydrocarbons produced during the hydrogen treatment at 260 °C. The hydrocarbons are C₁ to C₅ and

the number of carbon in the hydrocarbons decreases with time on stream. Raising the temperature to 400°C, shows a peak of hydrocarbons, mainly methane with minor amounts of ethane. It should be mentioned that data depicted on the Fig. 8 belongs to the first 100 minutes treatment.

The results presented in Figs. 7 and 8 may suggest that some long chain hydrocarbons and partially hydrogenated carbonaceous materials are formed during the FT synthesis. The long chain hydrocarbons are hydrogenolysed during the hydrodehydrogenation at 260°C [17]. Hydrocarbon products of this step follows the same behavior as the hydrogenolysis products, a logarithmic decline in their rate of formation with carbon number. More refractory, partially hydrogenated carbonaceous materials are converted to methane and minor amounts of ethane during the temperature rise to 400°C under hydrogen flow. Part of regeneration of the catalyst after the second and third hydrogen treatment steps (Fig. 6) could be due to the removal of the long chain hydrocarbons and carbonaceous materials, that may have blocked the catalyst sites.

The amount of coke deposition on the unpromoted cobalt catalysts and those promoted with Re and Ru, after the third hydrogen treatment step, were measured using UOP 703 standard method [11]. The amounts of coke were 0.0022, 0.0043 and 0.0031 grams per gram of the catalyst for Co, CoRe and CoRu catalysts, respectively. Higher amount of coke formation in the CoRe and CoRu also can be another reason of higher deactivation rate of these catalysts as compared with Co catalyst. It should be noted that the coke formed in this set of experiments could not be removed at the third treatment step, i. e. at 400°C

Fig. 9 shows CO₂ selectivity variations with time on stream for Co, CoRe and CoRu catalysts. As the Co/Al₂O₃ catalyst is promoted by Ru, CO₂ selectivity does not change significantly, whereas it is almost doubled when promoted by Re. This may be attributed to higher tendency of Re for adsorption of CO and water-gas shift reaction [18], which leads to the production of more CO₂. Fig. 9 shows that carbon dioxide selectivity decreases with increasing the duration of FT synthesis for all the catalysts, however, the decrease for unpromoted catalyst is lower. The decrease of the CO₂ selectivity may be attributed to the decrease in water partial pressure, due a decrease in reaction rate. The decrease in the CO₂

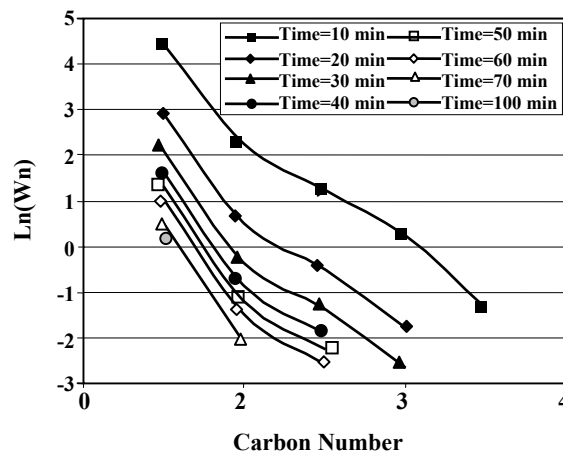


Fig. 8: Selectivity to different hydrocarbons during the hydrogen treatment of 1.4% Re promoted Co/Al₂O₃ catalyst with time on stream ($T=260^{\circ}\text{C}$, $P=1$ bar).

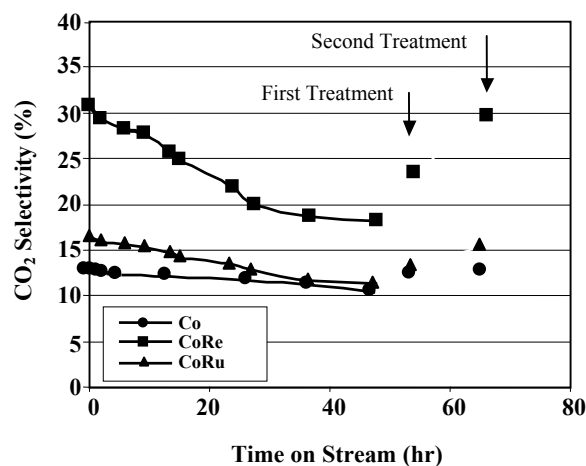


Fig. 9: CO₂ selectivity of catalysts with time on stream ($T=260^{\circ}\text{C}$, $P=1$ bar).

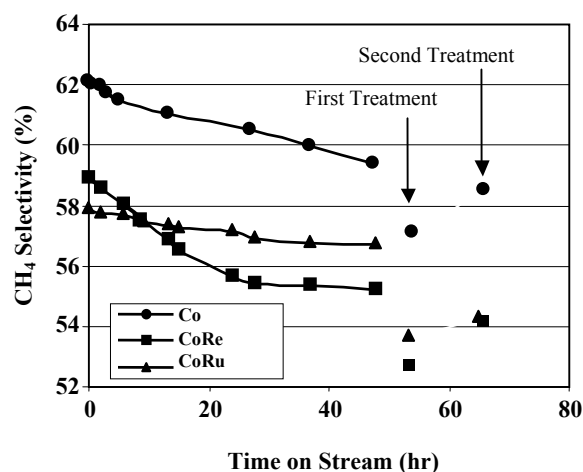


Fig. 10: CH₄ selectivity of catalysts with time on stream ($T=260^{\circ}\text{C}$, $P=1$ bar).

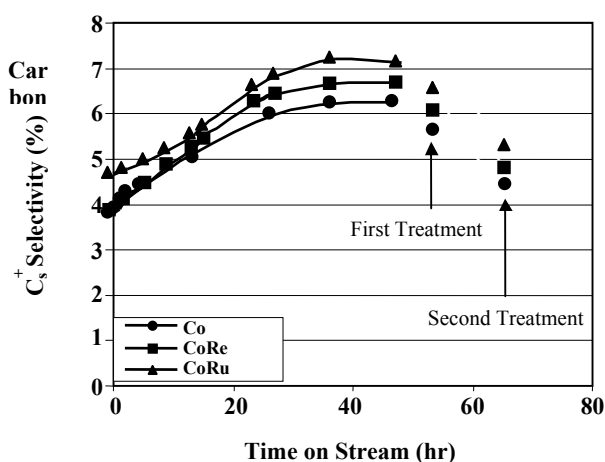


Fig. 11: C_5^+ selectivity of catalysts with time on stream ($T=260^\circ\text{C}$, $P=1\text{bar}$).

selectivity is concomitant with the decrease in the reaction rate of the catalysts (Fig. 6). Hydrogen treatment at 260 and 400°C, enhances both the FT synthesis rate and CO_2 selectivity (Figs. 6 and 9).

Figs. 10 and 11 show the methane and C_{5+} selectivity variations with reaction time for Co, CoRe and CoRu catalysts. For fresh catalysts, the methane selectivity decreases and C_{5+} selectivity increases in the order of $\text{Co} < \text{CoRe} < \text{CoRu}$. Fig. 10 displays that, for all the catalysts, CH_4 selectivity decreases with time on stream in the 48 h FT synthesis at 260°C, while the C_{5+} selectivity increases at the same time (Fig. 11). The CH_4 selectivity of CoRu catalyst slightly decreases during the 48 h synthesis, while that for the CoRe shows a sharp decrease in CH_4 selectivity upto about 24 h, then levels off. At the same time, for the unpromoted catalyst, there is a monotonous decrease in CH_4 selectivity. After the second hydrogen treatment at 260°C, the methane selectivity decreases for all the catalysts and the third hydrogen treatment at 400°C causes the methane selectivity to slightly increase.

Fig. 11 shows that the C_{5+} selectivity, for all the catalysts, increase until about 24 h, then level off. After the second hydrogen treatment at 260°C, C_{5+} selectivity decrease and the third hydrogen treatment at 400°C causes the C_{5+} selectivity to further decrease. Not shown here, the chain growth probability also follows the same trend as the C_{5+} selectivity. Fig. 12 shows the changes in 1-butene to n-butane ratio with time on stream. This ratio increases during the FT-synthesis and decreases in the

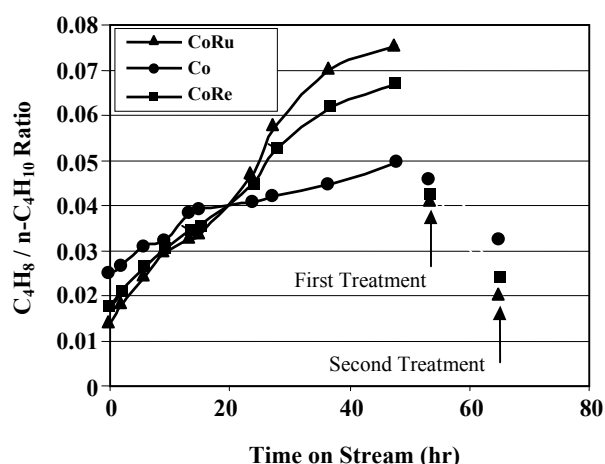


Fig. 12: $C_4H_8 / n-C_4H_{10}$ Ratio of catalysts with time on stream ($T=260^\circ\text{C}$, $P=1\text{bar}$).

hydrogen treatment steps.

One of the reasons for the selectivity changes may be the higher rate of deactivation of smaller cobalt particles. The larger cobalt particles are more selective to higher molecular weight hydrocarbons [12, 20, 21]. It is speculated that the smaller particles, selective for methane, are deactivated first, leading to enhancement of C_{5+} selectivity with time on stream. The slight decrease in methane selectivity, after mild hydrogen treatment at 260°C, suggest that the smaller cobalt particles are not regenerated in this treatment step. As was mentioned, the small catalyst particles interact more strongly with alumina as the support. The removal of heavy, probably unsaturated, hydrocarbons in the mild treatment enhances the termination rate of the catalyst, leading to lower C_{5+} selectivity. At the same time, the hydrogenolysis of the heavy hydrocarbons might be inhibited, resulting in lower methane selectivities.

CONCLUSION

The effects of Ru and Re as promoters on deactivation of $\text{Co}/\text{Al}_2\text{O}_3$ Fischer-Tropsch catalysts were investigated. The deactivation rates are higher in order of the Re-promoted > Ru-promoted > unpromoted cobalt catalysts. Activity loss was shown to have different sources; among them were: water-induced oxidation of cobalt, cobalt-alumina interactions, irreducible cobalt aluminates formation, sintering or cluster growth and finally refractory coke formation. The amount of activity recovery after treatment with hydrogen flow at low temperature treatment

at 260 °C and high temperature treatment at 400 °C for the used promoted and unpromoted catalysts were determined. High temperature H₂ treatment restored the catalytic activity of the catalysts to 98.8, 97.5 and 97.7% for Co, CoRe and CoRu respectively. Coke formation in Re promoted catalyst is about two times higher than that of the unpromoted catalyst and about 1.5 times higher as compared to Ru promoted catalyst.

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