

H₂-TPR, XPS and TEM Study of the Reduction of Ru and Re promoted Co/ γ -Al₂O₃, Co/TiO₂ and Co/SiC Catalysts

H. Romar^{1,3}, A. H. Lillebø², P. Tynjälä^{1,3}, T. Hu^{1,3}, A. Holmen², E. A. Blekkan² & U. Lassi^{1,3}

¹ University of Oulu, Research unit of Sustainable Chemistry, P.O.Box 3000, FI-90014 University of Oulu, Finland

² Norwegian University of Science and Technology (NTNU), Department of Chemical Engineering, NO-7491 Trondheim, Norway

³ University of Jyväskylä, Kokkola University Consortium Chydenius, Applied Chemistry, P.O.Box 567, FI-67101 Kokkola, Finland

Correspondence: U. Lassi, University of Oulu, Research unit of Sustainable Chemistry, P.O.Box 3000, FI-90014 University of Oulu, Finland. E-mail: ulla.lassi@oulu.fi

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Abstract

Effects of Ru and Re promoters on Co-CoO_x catalysts supported on γ -Al₂O₃, TiO₂ and SiC were investigated to improve the understanding of the role of promoters of the active phase of Co-CoO_x-Ru and Co-CoO_x-Re. The influence of promoter addition on the composition and activity of the catalysts was characterized by several methods, such as H₂-TPR, XPS, chemisorption and TEM. Furthermore, the role of support and metal-support interaction was especially studied and different support materials were compared.

Based on the results, addition of promoter metals (Ru or Re) will most likely improve catalytic activity of Co/ γ -Al₂O₃, Co/TiO₂ and Co/SiC catalysts by increasing the active metal surface available for chemical reaction and by decreasing the size of the metallic nanoparticles. These changes in the catalytic activity were also associated with the changes in the ratio of metal and metal oxide phases in the surface composition as observed by XPS. Promoter metals also decreased the reduction temperatures needed for the reduction of Co₃O₄ to CoO and further to metallic cobalt. Significant decrease in reduction temperature was observed especially when ruthenium was used as the promoter.

Keywords: catalyst, cobalt, Fischer-Tropsch, temperature-programmed reduction, TPR, XPS, TEM

1. Introduction

Cobalt catalysts are known to have a rather high activity in the Fischer-Tropsch (FT) reaction converting synthesis gas into hydrocarbons and waxes. Co catalysts have also proved to have a high selectivity to higher hydrocarbons (C₅₊) (Khodakov, Chu, & Fongarland, 2007; Khodakov, Holmen, Mirodatos, & Wang, 2013, Jean-Marie, Griboval-Constant, Khodakov, & Diehl, 2009). These catalysts have been supported by a number of supports, such as Al₂O₃, SiO₂ and TiO₂ (Adesina, 1996; Escalona et al., 2009, Borg, et al., 2007, de la Osa, et al., 2011).

The use of the Fischer-Tropsch reaction in the catalytic conversion of synthesis gas produced by biomass gasification is an interesting opportunity to produce transportation fuels as an alternative to fossil fuels presently used. In this, highly active and selective cobalt catalysts are needed, and therefore, understanding of metal-support interactions and the role of promoting metals is extremely important.

Noble metal promoters can generally act in three different ways or in combinations of these in catalytic reactions, i.e. (1) as reduction promoters to enhance the reducibility of the active metal, (2) as structural promoters to give a better dispersion of the active metal and (3) as electronic promoters to enhance the transportation of electrons between the support and the active metal. Moreover, the addition of noble metals to the catalyst can prolong the lifetime of the catalysts by preventing the formation of carbon deposits on the surface of the catalysts. Some promoter metals, such as ruthenium can also act as a catalytic metal in the Fischer-Tropsch reaction, but is not commercially used because of the high price of the metal (Ma et al., 2012, Kogelbauer Jr. et al., 1996, Xiong et al., 2009).

Activity and selectivity of the Fischer-Tropsch catalyst depend on a number of properties of the catalyst, e.g. metals and supports used, size of the supporting particles, dispersion of the active metal and the size of the metal particles

on the surface of the support. Factors decreasing the activity of the catalyst are impurities in the feed gas, alkali metal residues in the support or deposits from the syngas, and a poor dispersion of the active metal in the catalyst including sintering of the metal during catalyst use. (Borg et al., 2007, Lillebø et al., 2013, Cook et al., 2012).

The activity and also the selectivity of catalysts for FTS is related to the size of the Co crystals within certain particle sizes. Using catalysts with Co particles 10 to 200 nm in size the FTS activity is independent on the size of the Co particles (Rytter et al., 2007, Borg et al., 2008, Storsæter et al., 2005, Shetty & Van Santen, 2011). Furthermore, the selectivity against C_{5+} is rather independent of the particle size in the region 10-200 nm even if a slightly increased selectivity against CH_4 has been observed for the largest particles of 200 nm (Storsæter et al., 2005).

When it comes to smaller Co-particles from 1 to 10 nm there seems to be a linear relationship between the activity of the catalysts and the particle size (Borg et al., 2008). On the other hand, opposite effects have been reported by other researchers (den Breejen et al., 2009). The differences in data might be a result of the fact that when it comes to small particles less than 10 nm in size, it is difficult to separate the effects of metallic particles and the effects from the supports used (Frey, 2008). One possible solution to this is that the effects of the supports can be eliminated using model systems with carbon nanotubes as support (Bezemer et al., 2006, den Breejen et al., 2009).

This size effect can be explained with the fact that the most active parts of the crystal are those with high coordination numbers such as corners, steps or dislocations at the crystal surface which are not present if the crystals are too small. The effect of steps and corners on the dissociation of CO on Rh surfaces have been previously investigated by (Mavrikakis et al., 2002).

Impurities in the gas feed can be removed by the use of proper methods for gas cleaning, whereas alkali metals in supports can be avoided by screening of commercially available supports. One of the most demanding steps in the preparation of FT catalysts is to achieve a high dispersion of the active metal. Addition of small amounts of noble metals such as rhenium and ruthenium as promoters is known to improve the reducibility of the metal, leading to higher dispersion. The effects of promoter metals have been investigated in a number of studies (Cook et al., 2012, Borg et al., 2007, Borg et al., 2009) but most of these studies have been performed on catalysts prepared on a single support. In the present study, metal-support interactions and the effect of promoting metals (Re, Ru) on the reducibility of the cobalt catalysts are studied. Cobalt catalysts (15-20 wt%) were supported by aluminum oxide ($\gamma-Al_2O_3$), titanium dioxide (TiO_2) and silicon carbide (SiC). The role of support and support-metal interactions is especially studied while different support materials are compared.

2. Materials and methods

2.1 Catalysts and Catalyst Preparation

A series of unpromoted and promoted Co catalysts for Fisher-Tropsch synthesis were prepared and characterized. The catalysts were prepared with three supports. The alumina support material $\gamma-Al_2O_3$ (Sasol Puralox SSCa) was provided by Sasol, Germany. According to the manufacturer (Sasol Germany) the size distribution of alumina particles was 60-150 μm and the specific area was 90-210 m^2/g . The SiC support (β -SiC UHP3 LO) was provided by SiCat while the TiO_2 powder (Degussa P-25) was provided by Degussa.

Cobalt catalysts were prepared by the incipient wetness impregnation method in a one step process. The salts or solutions of the precursors ($Co(NO_3)_2 \cdot 6H_2O$, $Ru(NO)(NO_3)_2$ or perrhenic acid $HReO_4$) were dissolved and mixed in distilled water used in volumes equal to the pore volumes of the supports used. Prior to incipient wetness impregnation the supports were dried at 105°C for 2 hours in order to remove any water present in the pores. Impregnation time was 16 hours by mixing the support materials with metal salts dissolved in distilled water. Cobalt was used as an active metal in all catalysts in concentrations of 15 or 20wt%. 2 different metals (ruthenium, rhenium) were used in the concentrations of 0, 0.2, or 1.0 wt%.

After incipient impregnation the catalysts were dried, first at sub-atmospheric pressure at 60 °C for 30 minutes followed by 2 hours at 105 °C. The dried catalysts were calcined in static air at 420 °C for 16 hours with an initial temperature rise of 100°C/hour. Catalysts were sieved and a fraction of 50-100 μm was used for further experiments. Catalysts used in this study are denoted as follows: Support-Cobalt content-Ruthenium or Rhenium content. Supports are abbreviated with the following symbols: A = Al_2O_3 , S= SiC and T = TiO_2 . Therefore, a catalyst denoted A20Re0.2 contains 20 wt% Co and 0.2 wt% rhenium supported on Al_2O_3 .

2.2 Catalyst Characterization

Calcined catalysts were characterized by a number of techniques, e.g. surface area and pore size measurements by physisorption (Micromeritics ASAP2020), metal dispersion and metal surface area by CO chemisorption (Micromeritics ASAP2020), metal content by ICP-OES (Perkin Elmer Optima 5300 DV), and solid phases by X-ray diffraction (Siemens D5000 XRD device). Furthermore, temperature-programmed reduction (H_2 -TPR), XPS

and TEM were used for characterization of the catalyst. Based on the characterizations, activity and selectivity of catalysts in the Fischer-Tropsch reaction was determined for the most promising catalysts in which the results from the activity and selectivity measurements are published elsewhere (Romar et al., 2015).

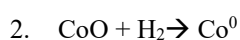
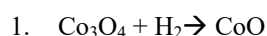
Specific surface area and pore distributions were determined from the adsorption-desorption isotherms. Determinations were performed with a Micromeritics ASAP 2020 instrument. Portions of each catalyst (about 200 mg) were pretreated at low pressures and high temperatures in order to clean their surfaces. Adsorption isotherms were obtained by immersing sample tubes in liquid nitrogen (-196 °C) in order to obtain isothermal conditions. Nitrogen was added to the samples in small steps and the resulting isotherms were obtained. Specific surface areas were calculated from adsorption isotherms according to the BET (Brunauer, Emmett et al. 1938) method, while nitrogen adsorption and desorption isotherms were used to calculate the pore size distribution using the BJH method (Barrett et al., 1951).

Chemisorption measurements were performed on a Micromeritics ASAP 2020 using CO as the adsorbate gas. About 500 mg of each catalyst was weight into a U-shaped tube of quartz glass in which the sample was supported on both sides by quartz wool. The samples were first evacuated and then reduced in a flow of H₂, first at a temperature of 110°C for 30 min followed by reduction at 350°C for 2 hours. Temperature rise was 10°C/min. After reduction of the samples the temperature was lowered to 40 °C, the tubes were evacuated and small pulses of CO were adsorbed onto the Co surface. Metal dispersions and sizes of the Co metal particles were calculated by assuming an average stoichiometry of 2:1 between cobalt and CO (Borg et al., 2009).

Transmission electron microscopy (TEM) was used for high magnification imaging of the catalyst microstructure. The microstructure images were taken by an energy filtered transmission electron microscope EFTEM (LEO 912 OMEGA EFTEM). The catalysts samples were dispersed in acetone and pretreated in an ultrasonic bath for several minutes, then added onto a carbon coated copper grid. The accelerating voltage and emission current in the measurements were 120 kV and 8-15 µA, respectively while the resolution of the instrument was 0.37 nm. The particle size of the samples was measured from 3-5 TEM images of each sample and give a reasonable range.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Fisher Scientific ESCALAB 250Xi XPS System at the Center of Microscopy and Nanotechnology, University of Oulu (Finland). The catalyst samples were placed on an Indium film. With pass energy of 20 eV, spot size of 900µm, the accuracy of the reported binding energy was ±0.2 eV. The Al, O, Co, Re or Ru, C, In and N were measured for all samples. The measurement data were analyzed by CasaXPS Version 2.3.16 PR 1.6. C_{1s} (284.6 eV) was used as a standard reference for calibration of all the samples.

H₂-TPR (temperature-programmed reduction) measurements were performed on a Quantachrome 3000 using 7% H₂ in Ar as the reducing gas. Measurements were performed by weighing 100 mg of each catalyst into a U-shaped quartz tube equipped with a temperature sensor. The temperature inside the reactor was elevated from 50 °C to 800 °C with a rise of 10 °C /min. The signal from the TC-detector was plotted against the reactor temperature. After the measurements the individual signals were processed using deconvolution and integration packages in the Quantachrom TPRWin software version 3.51. The peaks from the integration process are labeled as Peak 1 and Peak 2 respectively. Peak 1 represents the H₂ consumption for reaction (1) and Peak 2 represents the corresponding H₂ consumption for reaction (2). The effect of addition of promoter metals was calculated from the normalized peak areas. The individual peaks for the unpromoted catalysts were set to 100%, while the peaks for the promoted catalysts were calculated as % of these values.



3. Results and Discussions

3.1 Catalyst Characterization

Table 1 presents the results of catalyst characterization of unpromoted and Re/Ru promoted supported Co catalysts. Based on these results, it can be concluded that the addition of promoter metals (Ru or Re) improved the catalyst properties by increasing the active metal surface area available for chemical reaction and by decreasing the size of metallic Co nanoparticles. As can be seen in Table 1, the dispersion values for metallic Co on different supports are rather low, which is consistent with the dispersion levels of 2-6 % reported in literature (Ma et al., 2012, Jacobs et al., 2004).

Table 1. Characterization results of unpromoted and Ru/Re promoted Co/Al₂O₃, Co/SiC and Co/TiO₂ catalysts

Catalyst*	Surface area m ² /g	Pore volume (cm ³ /g)	Average pore diameter (nm)	Co dispersion (%)	Co metal particle size (nm)	Co metal surface area (m ² /g sample)	Co metal surface area (m ² /g of metal)
Al ₂ O ₃	195	0.52	10.6				
A20	117	0.31	10.8	1.0	96	1.4	10.6
A20Re0.2	125	0.31	9.7	5.0	19.2	6.8	34.0
A15Re0.2	126	0.34	10.8	5.0	19.2	5.0	33.4
A20Re1	106	0.26	9.8	7.0	13.7	9.6	45.6
A15Re1	121	0.29	9.4	8.6	11.2	8.8	58.0
A20Ru0.2	118	0.30	10.3	n.d.	n.d.	n.d.	n.d.
A15Ru0.2	133	0.36	10.7	2.2	43.6	2.2	14.4
A20Ru1	149	0.37	9.9	n.d.	n.d.	n.d.	n.d.
A15Ru1	124	0.31	10.0	6.6	14.5	6.4	43.2
SiC	25	0.15	24.0				
S20	20	0.13	26.5	1.2	80.0	1.6	8.0
S20Re0.2	29	0.12	16.3	3.2	30.0	3.2	21.0
S15Re0.2	29	0.29	40.6	2.8	34.2	3.0	19.4
S20Ru0.2	22	0.14	26.4	2.0	48.0	2.6	13.2
S15Ru0.2	19	0.12	25.2	2.8	34.2	3.6	23.4
TiO ₂	54	0.18	13.5				
T20	25	0.23	36.6	1.2	80.0	1.2	7.8
T15Re0.2	29	0.12	16.3	2.6	36.9	2.6	17.0
T20Re0.2	30	0.24	33.0	4.8	20.0	6.6	32.6
T15Ru0.2	36	0.27	30.2	7.6	12.6	7.6	51.4
T20Ru0.2	38	0.28	29.8	n.d.	n.d.	n.d.	n.d.

*In Table 1, A, S and T denote to Al₂O₃, SiC and TiO₂ supports respectively. Corresponding values are metal concentrations for Co (15 or 20 wt%) and promoting metals (Ru or Re) of 0.2 or 1 wt%.

The surface areas of supports (195 m²/g for Al₂O₃; 25 m²/g for SiC and 25 m²/g for TiO₂) were higher prior to impregnation of metals, as expected. By assuming that the total surface areas comes from the supports the addition of 20 mass % of cobalt would lead to a corresponding 20% decrease in specific surface areas (Das et al., 2003, Jacobs et al., 2014). This would lead to the surface areas of 156 m²/g for Al₂O₃, 20 m²/g for SiC and 20 m²/g for TiO₂ for the catalysts with 20 mass % Co.

Correspondingly to the surface areas of 165 m²/g for Al₂O₃, 21 m²/g for SiC and 21 m²/g for TiO₂ for the catalysts with 15 mass % Co. The measured values are slightly below the measured surface area of the support prior to impregnation with metals, a fact that indicates some degree of pore clogging. The one-step impregnation used in the catalyst preparation might be the main reason for this phenomenon, since similar catalysts were prepared with a three-step impregnation without any loss of specific surface area (Jacobs et al., 2004). For the SiC supported catalysts an increase in the mean pore size is noticed, this can be explained by clogging, totally or partially, of minor pores shifting the mean value for the pore size to larger values.

TEM images of some catalyst samples are presented in Figure 1. The Al₂O₃ supported catalysts A20, A15Re0.2 and A15Ru0.2 are shown in Figures 1(a), 1(b) and 1(c). The particle sizes of Co are 5-10 nm, which are seen in Figure 1(a) while other samples containing Co and Re or Ru have similar metal particles sizes. An exception to

this is the sample A15Ru0.2 where bigger metal particles in the range of 20-80 nm are found (Figure 1(c)). It should also be noted that it was difficult to distinguish Co with Re or Ru particles in TEM images. The crystalline size of the samples A20, T20 and S20 were measured from XRD pattern in our previous research with value of 5.5 nm, 18 nm and 33 nm, respectively (Romar et al., 2015).

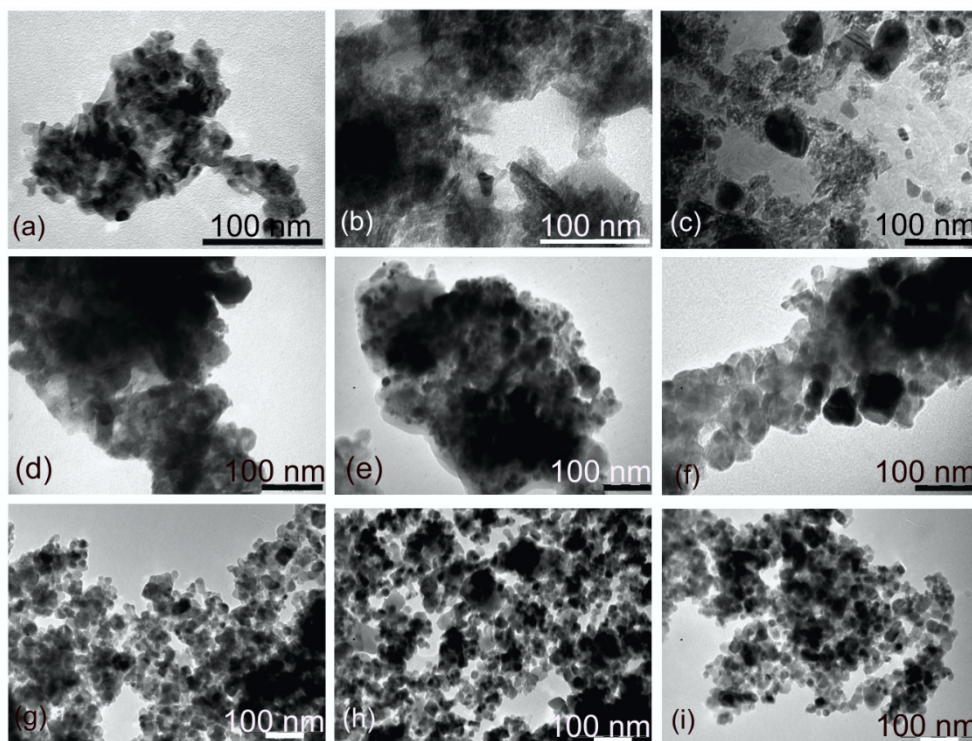


Figure 1. TEM images of a) A20, b) A15Re0.2, c) A15Ru0.2, d) S20, e) S15Re0.2, f) S15Ru0.2, g) T20, h) T15Re0.2, and i) T15Ru0.2 catalysts

For some catalysts supported on alumina, there is some discrepancy in the results obtained with different methods for the determination of metal particle sizes. Determination of cobalt particle size by TEM usually gives smaller particles than the same measurement performed by chemisorption. The TEM measurements were performed on samples with cobalt in oxide form. It appears that the metallic cobalt crystallites after reduction are reduced in size by approximately 40% compared to the initial phase as reported by Rønning et al. (2010). This phenomenon can especially be seen for the catalyst A20 where measurements by chemisorption gives a particle size of 20-80 nm whereas for TEM measurements they are 5-10 nm. For the promoted catalysts the TEM images gives slightly smaller particles compared to the results obtain by chemisorption, these results are more in agreement with each other compared to the results obtained from the unpromoted catalysts. Based on both the results from TEM and chemisorption of carbon monoxide the addition of promoter metals such as ruthenium and rhenium increases the dispersion of the active metal, in this case cobalt.

The SiC supported samples S20, S15Re0.2 and S15Ru0.2 are shown in Figures 1(d), 1(e) and 1(f). Most of the catalysts particles were in range of 5-10 nm while a few bigger particles of 50-80 nm were also observed. As mentioned above, for alumina supported catalysts similar results can be seen compared to SiC supported catalysts. The sizes of the cobalt particles in the unpromoted catalyst S20 is much larger in TEM measurements compared to the ones from chemisorption measurements, mostly 5-10 nm even if some larger particles are detected compared to the 169 nm particles found by chemisorption of CO. The effects of the promoting metals ruthenium and rhenium is not as obvious as for the alumina supported catalysts, the particle sizes are generally larger especially from the chemisorption results, in the SiC supported catalyst compared to the alumina supported ones.

TEM images of TiO₂ supported samples T20, T15Re0.2 and T15Ru0.2 are presented in Figures 1(g), 1(h) and 1(i). It is more difficult to identify the catalysts particles from the TiO₂ particles because of a similar crystallite shape. However, it is easier to detect that in Figure 1(g) smaller particles in the range of 5-10 nm existed in catalysts samples than in pure TiO₂ samples.

The same effect as for the other supports can be observed with the TiO₂ supported catalysts. Unpromoted Co-catalysts have much larger particles than the ones promoted with ruthenium and rhenium. A comparison of the catalysts with same metal loadings on three different supports results in the order Al₂O₃>TiO₂>SiC when it concerns the particle size for the unpromoted catalysts with 20 mass-% cobalt.

3.2 H₂-TPR

The results from the H₂-TPR measurements over Al₂O₃, TiO₂ and SiC supported catalysts are presented in Figure 4. A plot of the TPR-signals vs. temperature typically shows three distinct peaks. The first small peak (at temperature of 280°C, for catalyst A20) results from the reduction of traces of nitrates from the precursor salt. The main peaks in the TPR-signal (at 450°C and 540 °C for catalyst A20) represent the reduction of Co₃O₄ to CoO and further to Co⁰. In some cases the distinct 2-step reduction via CoO can be observed, in other cases the second peak also represents the reduction of different Co²⁺ and Co³⁺ species stabilized by the interaction with the support. Addition of small amounts of promoters (Re or Ru) decreases the reduction temperature of cobalt oxide. This is indicated by a shift of the TPR peaks to lower temperatures compared to the signal from a catalyst containing only Co as described in Table 2 for catalysts containing 20 mass-% Co. While Re mainly shifts the second peak, Ru shifts the position of both peaks to lower temperatures. This is reasonable, given the reduction temperatures of the two metal oxides. The interaction between the support and the metal oxides has a strong influence on the reducibility of the cobalt oxide, this interaction can be seen from the fact that the reduction process on Al₂O₃ is not complete even at 800°C.

Table 2. Temperatures (°C) for the reduction steps of catalysts containing 20 mass-% Co

Catalyst	Co ₃ O ₄ →CoO	CoO→Co ⁰
A20	450	540
A20Re0.2	410	690
A20Ru0.2	325	650
S20	425	500
S20Re0.2	425	500
S20Ru0.2	300	450
T20	450	575
T20Re0.2	390	460
T20Ru0.2	310	500

Besides the shift of the reduction peaks to lower temperatures the addition of small amounts of promoter metals like Ru and Re leads to an increased dispersion of the active metal (Co) and an increase in the surface of Co making more of the metal available for chemical reaction (see Table 1). Most likely there is an increase in the degree of reduction of the metal even if this effect not has been investigated in this study.

The effects of addition of promoter metals on the consumption of H₂ during the reduction steps are presented in Table 3 and equations 1 and 2. In the Table the consumption of H₂ for each unpromoted catalyst is set to be 100% and the relative H₂ consumption for the promoted catalysts are calculated as % of this value. As can be seen there is a decrease in H₂ consumption for the promoted catalysts, the effect is most obvious for the catalyst supported on Al₂O₃. For the Al₂O₃ supported catalysts Ru seems to be more effective in enhancing the reduction of cobalt than Re. This is especially pronounced in the first step of the reduction process and the effect of Ru promotion can, as earlier mentioned, also be seen as a reduction at lower temperatures. Furthermore, for 1 wt% Ru, a concentration much higher than normally used for promoter metals has a very dramatic effect on the H₂ consumption, again this effect is most evident at the first step.

The relations between the two peaks are also presented in Table 3. Theoretically the ratio should be 3, but the second peak is in many cases is too low, indicating the lower degree of reduction in the second step of the reduction process. Due to the slow reduction resulting in lagging peaks for the second step for some of the catalysts there might be some problems with integrations, especially of the second peak for catalysts such as A20Re0.2 and T20Re0.2.

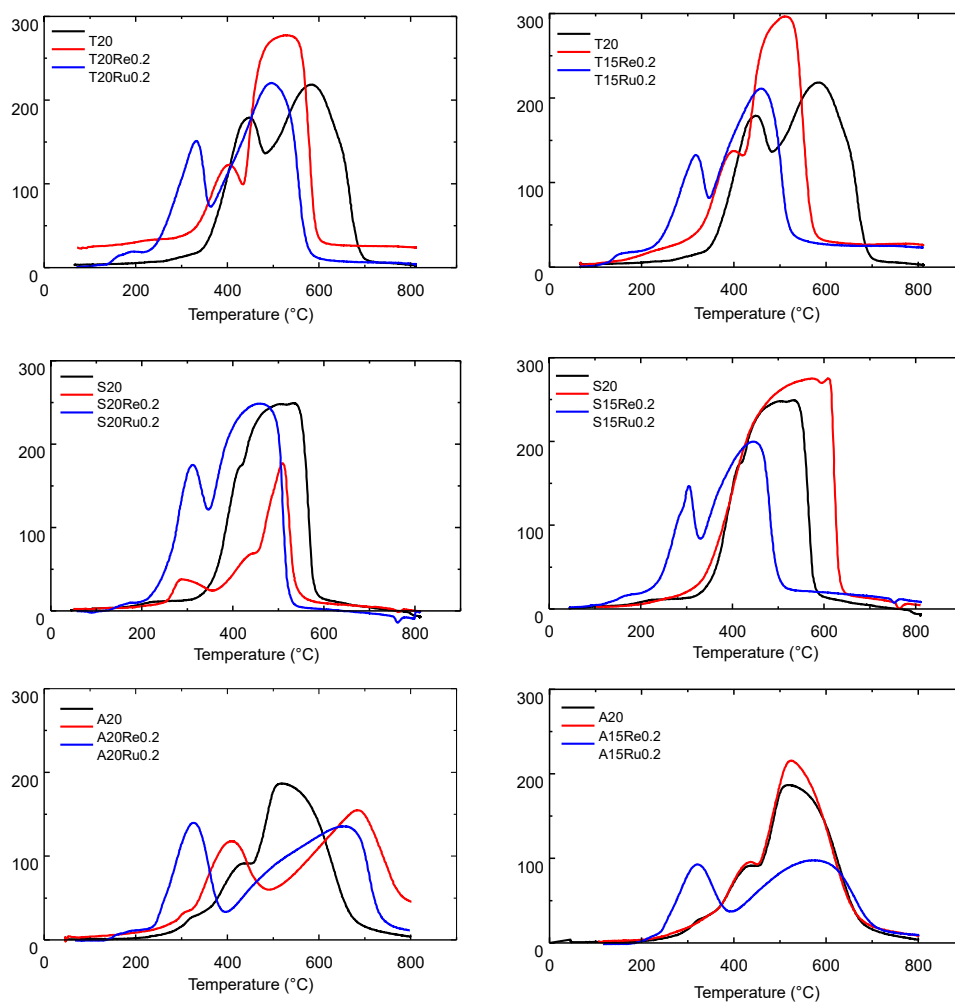


Figure 2. H_2 -TPR of promoting metals (Re and Ru) on the reducibility of Co-catalysts supported by Al_2O_3 , SiO₂ and TiO₂

3.3 XPS

XPS spectra of Al_{2p} , Co_{2p} and O_{1s} for the sample A15Re1 are shown in Fig. 3 as an example. The total scanning range for the survey was 0-1350 eV (Fig. 3a). The binding energy of Al_{2p} showed two peaks with maximum centered at 77.9 eV and 73.5 eV (Fig. 3b) which is typical from Al_2O_3 . In Fig. 3c the binding energy of Co_{2p} revealed a broad peak with a maximum centered at 779.7 eV for $Co_{2p_{3/2}}$, which indicates the bulk of cobalt is Co_3O_4 according to the report of Jacobs G. et al. (Jacobs, Chaney et al. 2004). The O_{1s} core level spectra had one peak with a BE of 530.2 eV which is corresponding to the lattice oxygen in Al_2O_3 (Fig.3d).

XPS spectra of the Ru-promoted catalysts with 15 wt% of Co are presented in Fig. 4, including T15Ru0.2, S15Ru0.2, A150.2 and A15Ru1. Unfortunately, the $Ru_{3d_{3/2}}$ (284.8eV) spectra were overlapped with C_{1s} (284.6 eV) and therefore difficult to identify. $Ru_{3d_{5/2}}$ (279.3eV) spectra for samples with Ru of 0.2 wt% were not detected due to the low concentration of Ru. The $Ru_{3d_{5/2}}$ spectra for the sample with Ru of 1 wt% (A15Ru1) can be identified which is shown in Figure 4(b). The binding energy of $Ru_{3d_{5/2}}$ was 279.3 eV, which was the same value for A20Ru1.

XPS spectra for all the Al_2O_3 supported catalysts with Ru additions were compared and are presented in Figure 5a, which indicates that the addition of Ru does not affect the position of $Co_{3/2}$ peaks much. The binding energy of maximum centered $Co_{2p_{3/2}}$ were in the range of 778.5-779.3 eV. Fig. 5b showed the results for the Al_2O_3 supported catalysts added with Re promoter. The $Co_{3/2}$ peaks for all Re-promoted samples were similar and quite broad. The $Co_{2p_{3/2}}$ had maximum centered at BE value of 794.0-796.1 eV.

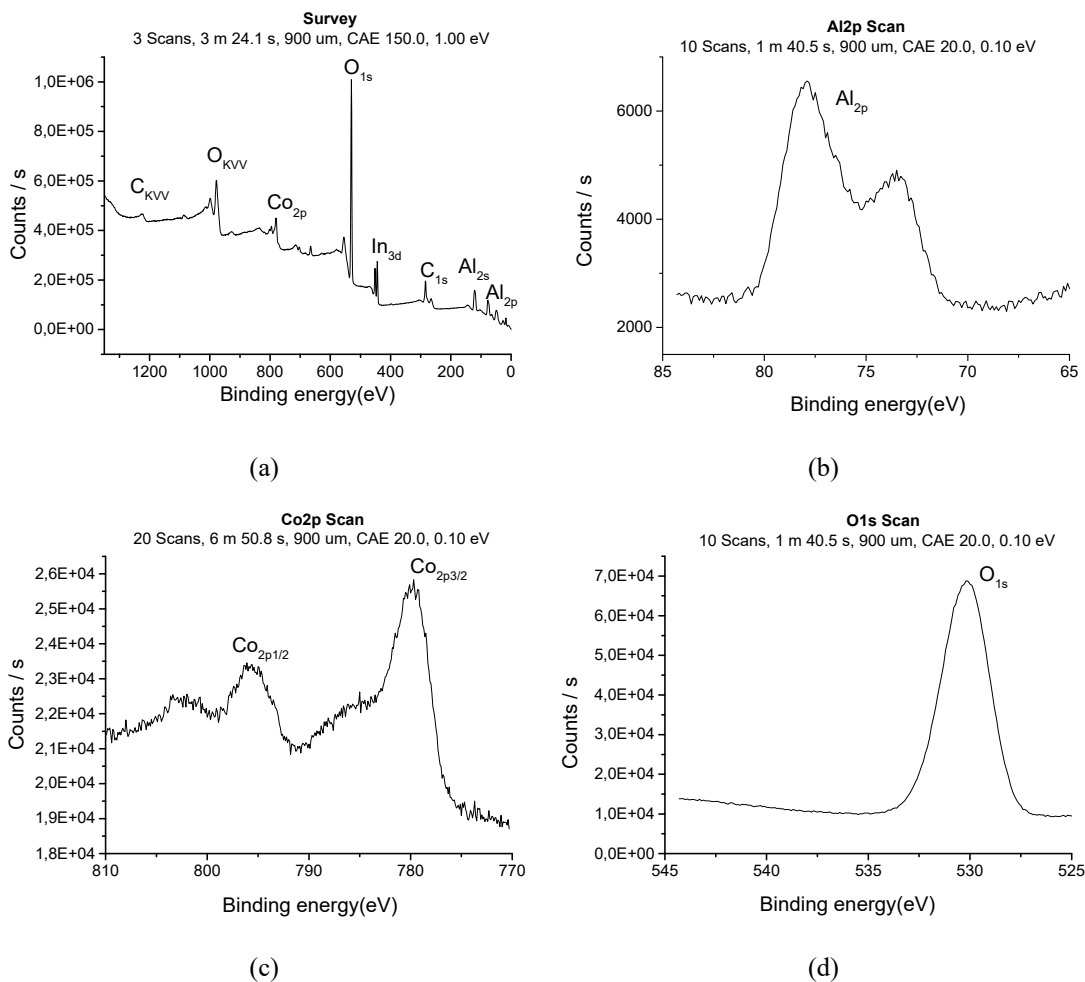


Figure 3. XPS spectra of Al 2p, Co 2p, O 1s core level in A15Re1

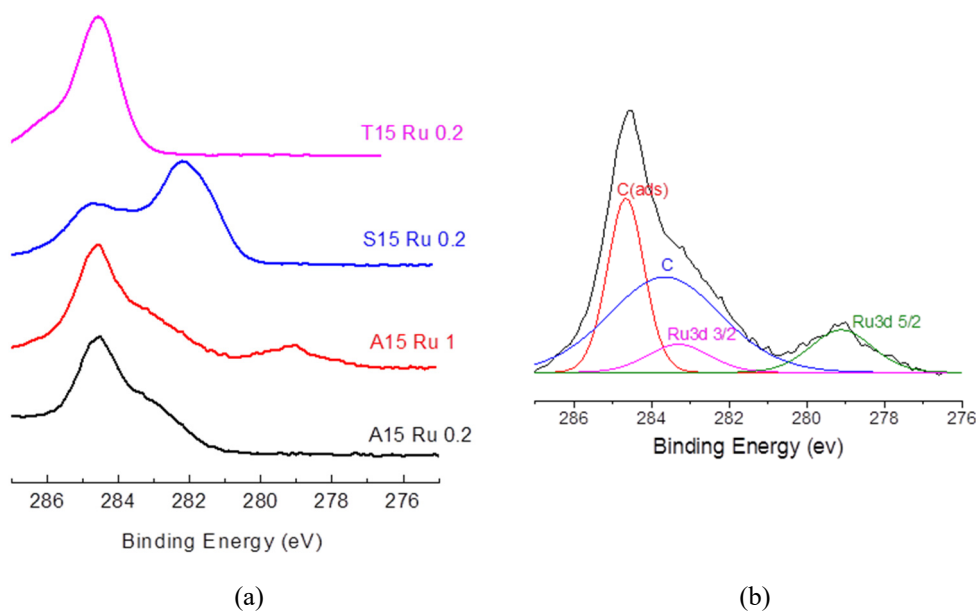


Figure 4. XPS spectra of a) Ru-promoted catalysts, and b) fitting for A15Ru1 catalyst

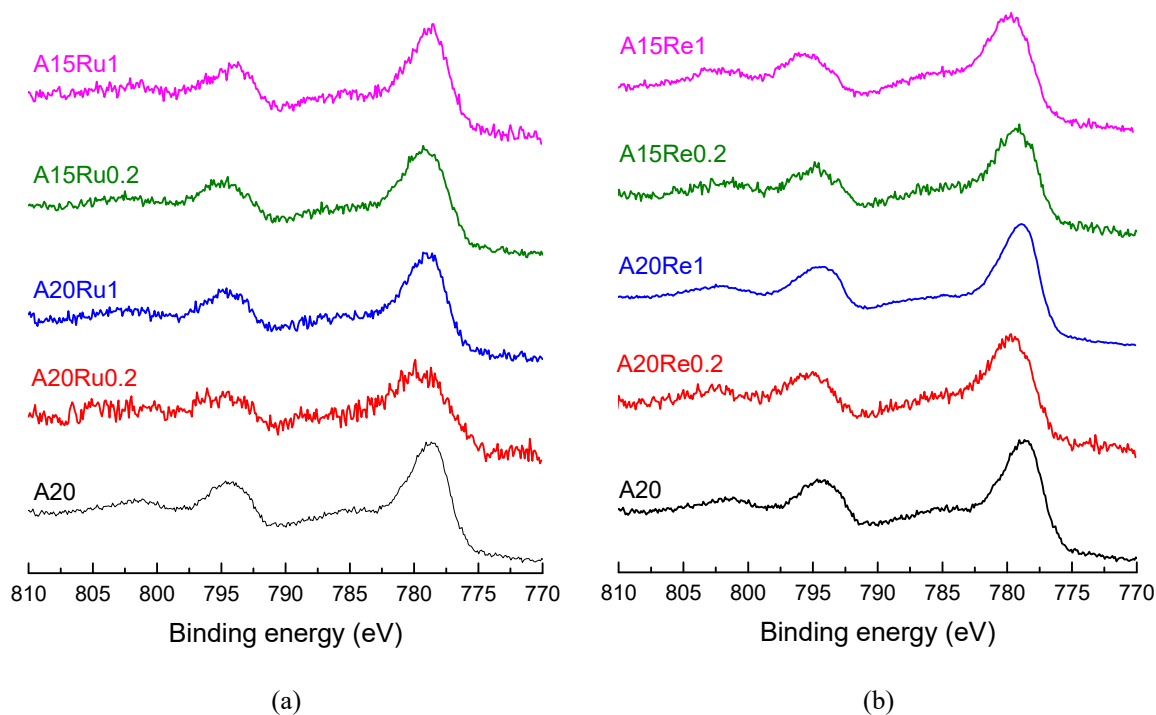


Figure 5. XPS spectra for $\text{Co}_{3/2}$ of Al supported samples with different a) Ru and b) Re additions

4. Conclusions

As catalysts for the Fischer-Tropsch conversion of synthesis gas into transportations fuels like diesel, supported cobalt or iron catalysts have been used. In this study a number of cobalt catalysts were prepared using three types of supports; γ -alumina oxide, silicon carbide and titanium dioxide. The catalyst were promoted with ruthenium or rhenium, or used without any promoting metal.

From the results it is obvious that the use of promoter metals like Ru and Re in cobalt based catalysts have several effects on the properties of the catalyst. From the results obtained we can see an increase in the dispersion of the metallic cobalt particles, as an effect of increased dispersion the particles are smaller in the promoted catalyst. This dispersion effect can be observed for all supports used in this study even if it is more pronounced for the catalysts supported by alumina oxide. These preliminary results from the characterizations indicate that some of the catalysts and calcined prepared and calcined might be highly active in the Fischer-Tropsch synthesis of traffic fuels according to their properties. So far no tests for the activities and selectivities of the catalysts have been performed but the catalysts are, however, subject for further investigations.

The reduction of cobalt is affected by the addition of promoter metals as described in the TPR results. The effect of promoters can be seen as a decrease in H_2 consumption during the reduction steps. This effect is most pronounced for the catalysts supported on $\gamma\text{-Al}_2\text{O}_3$ and SiC whereas the effect can be seen for Ru promoted catalysts only when supported on TiO_2 . For all supports there is a small decrease in the surface area measured indicating some clogging of the pores. This effect is most obvious for the catalysts supported by TiO_2 and $\gamma\text{-Al}_2\text{O}_3$.

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References

- Adesina, A. A. (1996). Hydrocarbon synthesis via Fischer-Tropsch reaction: travails and triumphs. *Applied Catalysis A: General*, 138(2), 345-367. [http://dx.doi.org/10.1016/0926-860X\(95\)00307-X](http://dx.doi.org/10.1016/0926-860X(95)00307-X)

- Barrett, E. P., Joyner, L. G., & Halenda, P. P. (1951). The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *Journal of the American Chemical Society*, 73(1), 373-380.
- Bezemer, G. L., Bitter, J. H., Herman P. C. E., Kuipers, H. P. C. E., Oosterbeek, H., Holewijn, J. E., De Jong, K. P. (2006). Cobalt Particle Size Effects in the Fischer-Tropsch Reaction Studied with Carbon Nanofiber Supported Catalysts. *Journal of the American Chemical Society*, 128, 3956.
- Borg, Ø., Dietzel, P. D. C., Spjelkavik, A. I., Tveten, E. Z., Walmsley, J. C., Diplas, S., ... Rytter, E. (2008). Fischer-Tropsch synthesis: Cobalt particle size and support effects on intrinsic activity and product distribution. *Journal of Catalysis*, 259(2), pp. 161-164. <http://dx.doi.org/10.1016/j.jcat.2008.08.017>
- Borg, Ø., Eri, S., Blekkan, E. A., Storsæter, S., Wigum, H., Rytter, E., & Holmen, A. (2007). Fischer-Tropsch synthesis over γ -alumina-supported cobalt catalysts: Effect of support variables. *Journal of Catalysis*, 248(1), 89-100. <http://dx.doi.org/10.1016/j.jcat.2007.03.008>
- Borg, Ø., Hammer, N., Eri, S., Lindvåg, O. A., Myrstad, R., Blekkan, E. A., ... Holmen, A. (2009). Fischer-Tropsch synthesis over un-promoted and Re-promoted γ -Al₂O₃ supported cobalt catalysts with different pore sizes. *Catalysis Today*, 142(1-2), 70-77. <http://dx.doi.org/10.1016/j.cattod.2009.01.012>
- Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, 60(2), 309.
- Cook, K. M., Poudyal, S., Miller, J. T., Bartholomew, C. H., & Hecker, W. C. (2012). Reducibility of alumina-supported cobalt Fischer-Tropsch catalysts: Effects of noble metal type, distribution, retention, chemical state, bonding, and influence on cobalt crystallite size. *Applied Catalysis A: General*, 449, 69-80. <http://dx.doi.org/10.1016/j.apcata.2012.09.032>
- Das, T. K., Jacobs, G., Patterson, P. M., Conner, W. A., Li, J., & Davis, B. H. (2003). Fischer-Tropsch synthesis: characterization and catalytic properties of rhenium promoted cobalt alumina catalysts. *Fuel*, 82(7), 805-815. [http://dx.doi.org/10.1016/S0016-2361\(02\)00361-7](http://dx.doi.org/10.1016/S0016-2361(02)00361-7)
- De La Osa, A. R., De Lucas, A., Romero, A., Valverde, J. L., & Sánchez, P. (2011). Fischer-Tropsch diesel production over calcium-promoted Co/alumina catalyst: Effect of reaction conditions. *Fuel*, 90(5), 1935-1945. <http://dx.doi.org/10.1016/j.cattod.2011.12.029>
- Den Breejen, J. P., Radstake, P. B., Bezemer, G. L., Bitter, J. H., Frøseth, V., Holmen, A., & De Jong, K. P. (2009). On the Origin of the Cobalt Particle Size Effects in Fischer-Tropsch Catalysis. *Journal of the American Chemical Society*, 131, 7197-7203.
- Escalona, N., Medina, C., García, R., & Reyes, P. (2009). Fischer-Tropsch reaction from a mixture similar to biosyngas. Influence of promoters on surface and catalytic properties of Co/SiO₂ catalysts. *Catalysis Today*, 143(1-2), 76-79. <http://dx.doi.org/10.1016/j.cattod.2008.10.030>
- Frey, A. M. (2008). *Design of heterogenous catalysts*. PhD thesis, Center for Sustainable and Green Chemistry Department of Chemistry Technical University of Denmark.
- Jacobs, G., Chaney, J. A., Patterson, P. M., Das, T. K., & Davis, B. H. (2004). Fischer-Tropsch synthesis: study of the promotion of Re on the reduction property of Co/Al₂O₃ catalysts by in situ EXAFS/XANES of Co K and Re LIII edges and XPS. *Applied Catalysis A: General*, 264(2), 203-212. <http://dx.doi.org/10.1016/j.apcata.2003.12.049>
- Jacobs, G., Ma, W., & Davis, B. (2014). Influence of reduction promoters on stability of cobalt/ γ -Al₂O₃ Fischer-Tropsch synthesis catalysts. *Catalysts*, 4, 49-76. <http://dx.doi.org/10.3390/catal4010049>
- Jean-Marie, A., Griboval-Constant, A., Khodakov, A. Y., & Diehl, F. (2009). Cobalt supported on alumina and silica-doped alumina: Catalyst structure and catalytic performance in Fischer-Tropsch synthesis. *Comptes Rendus Chimie*, 12(6-7), 660-667.
- Khodakov, A. Y., Chu, W., & Fongarland, P. (2007). Advances in the Development of Novel Cobalt Fischer-Tropsch Catalysts for Synthesis of Long-Chain Hydrocarbons and Clean Fuels. *Chemical Reviews*, 107, 1692. <http://dx.doi.org/10.1021/cr050972v>
- Khodakov, A. Y., Holmen, A., Mirodatos, C., & Wang, Y. (2013). Catalysis and synthetic fuels: State of the art and outlook. *Catalysis Today*, 215, 1. <http://dx.doi.org.ezproxy.jyu.fi/10.1016/j.cattod.2013.07.017>
- Kogelbauer, A., Goodwin J. R., J. G., & Oukaci, R. (1996). Ruthenium promotion of Co/Al₂O₃ Fischer-Tropsch catalysts. *Journal of Catalysis*, 160(1), 125-133.

- Lillebø, A. H., Patanou, E., Yang, J., Blekkan, E. A., & Holmen, A. (2013). The effect of alkali and alkaline earth elements on cobalt based Fischer–Tropsch catalysts. *Catalysis Today*, 215, 60-66. <http://dx.doi.org.ezproxy.jyu.fi/10.1016/j.cattod.2013.07.017>
- Ma, W., Jacobs, G., Keogh, R. A., Bukur, D. B., & Davis, B. H. (2012). Fischer–Tropsch synthesis: Effect of Pd, Pt, Re, and Ru noble metal promoters on the activity and selectivity of a 25%Co/Al₂O₃ catalyst. *Applied Catalysis A: General*, 437–438, 1-9. <http://dx.doi.org/10.1016/j.apcata.2012.05.037>
- Mavrikakis, M., Bäumer, M., Freund, M., & Norskov, J. K. (2002). Structure sensitivity of CO dissociation on Rh surfaces. *Catalysis Letters*, 81(3-4), 153-156.
- Romar, H., Lillebø, A. H., Tynjälä, P., Hu, T., Holmen, A., Blekkan, E. A., & Lassi, U. (2015). Characterization and catalytic Fischer-Tropsch activity of Co-Ru and Co-Re catalysts supported on γ -Al₂O₃, TiO₂ and SiC. *Topics in Catalysis*, 58(14). <http://dx.doi.org/10.1007/s11244-015-0455-0>
- Rønning, M., Tsakoumis, N. E., Voronov, A., Johnsen, R. E., Norby, P., Van Beek, W., ... Holmen, A. (2010). Combined XRD and XANES studies of a Re-promoted Co/ γ -Al₂O₃ catalyst at Fischer–Tropsch synthesis conditions. *Catalysis Today*, (155), 289-295.
- Rytter, E., Eri, S., Hulsund Skagseth, T., Schanke, D., Bergene, E., Myrstad, R., ... Lindvåg, A. (2007). Catalyst Particle Size of Cobalt/Rhenium on Porous Alumina and the Effect on Fischer-Tropsch Catalytic Performance. *Industrial Engineering and Chemical Research*, 46, 9032-9036.
- Shetty, S., & Van Santen, R. A. (2011). CO dissociation on Ru and Co surfaces: The initial step in the Fischer–Tropsch synthesis. *Catalysis Today*, 171(1), 168-173. <http://dx.doi.org/10.1016/j.cattod.2011.04.006>
- Storsæter, S., Tøtdal, B., Walmsley, J. C., Tanem, B. S., & Holmen, A. (2005). Characterization of alumina-, silica-, and titania-supported cobalt Fischer–Tropsch catalysts. *Journal of Catalysis*, 236(1), 139-152. <http://dx.doi.org/10.1016/j.jcat.2005.09.021>
- Xiong, H., Zhang, Y., Liew, K., & Li, J. (2009). Ruthenium promotion of Co/SBA-15 catalysts with high cobalt loading for Fischer–Tropsch synthesis. *Fuel Processing Technology*, 90(2), 237-246. <http://dx.doi.org/10.1016/j.fuproc.2008.08.014>

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