

Study of the effect of water on Fischer–Tropsch synthesis over supported cobalt catalysts

S. Storsæter, Ø. Borg, E.A. Blekkan, A. Holmen*

Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

Received 12 November 2004; revised 28 January 2005; accepted 31 January 2005

Available online 23 March 2005

Abstract

The effect of water on the activity and selectivity of unpromoted and Re-promoted cobalt Fischer–Tropsch catalysts supported on Al_2O_3 , SiO_2 , and TiO_2 has been studied in a fixed-bed reactor at 483 K and 20 bar. Common for all the catalysts was an increase in C_{5+} selectivity and a decrease in the CH_4 selectivity at increased conversion or by external water addition. Promoting with Re increased the reaction rate [$\text{g}_{\text{HC}}/(\text{g}_{\text{cat}} \text{ h})$] for all catalysts and the C_{5+} selectivity for the SiO_2 - and TiO_2 -supported catalysts. It was found that the $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{CoRe}/\text{Al}_2\text{O}_3$ catalysts deactivate when water is added during Fischer–Tropsch synthesis. For the Co/SiO_2 and CoRe/SiO_2 catalysts the reaction rate increased with increasing conversion or upon water addition. However, at high concentrations of water the catalysts deactivate rapidly. An increased reaction rate was also observed for the Co/TiO_2 and CoRe/TiO_2 catalysts with increasing conversion or with the addition of small amounts of water. At higher partial pressures of water the reaction rate decreased. Water interacts with the catalysts in different ways, and the effect of water is discussed in terms of Co particle sizes, secondary reactions, adsorbed species on the catalyst surface, and diffusion in liquid-filled pores.

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Keywords: Fischer–Tropsch synthesis; Cobalt; Rhenium; Alumina; Silica; Titania; Water

1. Introduction

The Fischer–Tropsch synthesis is an interesting and promising pathway for the conversion of natural gas to transportation fuels. A key element in improved Fischer–Tropsch processes is the development of active catalysts with high wax selectivity. Supported cobalt is the preferred catalyst for the Fischer–Tropsch synthesis of long-chain paraffins from natural gas because of its high activity and selectivity, low water–gas shift activity, and comparatively low price. Water is produced during the Fischer–Tropsch synthesis and is present in varying quantities during the reaction, depending on the conversion and reactor system.

Different results have been reported for the effect of water on the Fischer–Tropsch activity for cobalt catalysts. It

has been observed that addition of water to Re-promoted or unpromoted $\text{Co}/\text{Al}_2\text{O}_3$ catalysts results in catalyst deactivation [1–3]. The observed deactivation is only partly reversible. The same effect has been found for Pt-promoted $\text{Co}/\text{Al}_2\text{O}_3$ catalysts [4]. Schanke et al. [3] examined the deactivation mechanism of Al_2O_3 -supported Co catalysts by model studies using $\text{H}_2\text{O}/\text{H}_2$ feeds in conjunction with XPS and gravimetry and found that reoxidation of surface cobalt or highly dispersed cobalt phases interacting with the support is the most likely reason for the observed deactivation. van Berge et al. [5] concluded from Mössbauer emission spectroscopy and thermogravimetry results that the degree of oxidation of Al_2O_3 -supported catalyst depends on the $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ratio. Jacobs et al. [6] concluded from XANES studies that for noble metal-promoted $\text{Co}/\text{Al}_2\text{O}_3$ catalysts, small Co clusters interacting with the support undergo oxidation in the presence of water and that significant cobalt cluster growth takes place during the initial period of deactivation.

* Corresponding author. Fax: +47 735 95047.

E-mail address: holmen@chemeng.ntnu.no (A. Holmen).

Indigenous or added water has been reported to increase the activity [7,8] and to decrease the activity [9] on Co/SiO₂ catalysts. At high conversions and high water partial pressures rapid deactivation is observed, but very slow deactivation is observed at low conversions [8,10] when no water is added. The loss of activity at high water partial pressures has been found to be irreversible and due to support breakdown by water accompanied by the formation of cobalt silicates [10].

For Re-promoted and unpromoted Co/TiO₂ catalysts both increased activity [11–14] and decreased activity [15] have been reported with increased partial pressure of water. Bertole et al. [11] explained the increased activity by water by suggesting that water induced an enhancement of the CO dissociation rate.

For a bulk Co catalyst [16] and a Co/MgO₂/ThO₂/Aerosil catalyst, water was found to increase the activity [17]. However, no effect was found on the effect of water on the activity for a Co/ZrO₂/Aerosil catalyst [18].

Even though water apparently influences the activity of various Co catalysts in different ways, water increases the C₅₊ selectivity and decreases the CH₄ selectivity for all Co catalysts [1,2,7,11,13,14,16–18]. Different explanations have been proposed to explain this effect, including the reduction of secondary hydrogenation of primary olefins by water [1,12,19], thereby facilitating olefin readsorption and chain initiation.

As discussed above, there have been contradictory observations of the effect of water on the performance of Co catalyst with different supports, and there does not seem to be an obvious common explanation of the observed effects. The purpose of the present work was to study the effect of water on the activity and selectivity for a series of cobalt catalysts using different supports. The effect of water is studied by making changes in the conversion and thereby increasing the partial pressure of water or with the addition of external water to the feed gas. By use of the same experimental procedures and the same reactor setup for all of the catalysts, a more reliable basis for comparisons is obtained.

2. Experimental

2.1. Catalyst preparation

Catalysts containing 12 wt% Co and 12 wt% Co–0.5 wt% Re were prepared by incipient wetness coimpregnation of different supports with aqueous solutions of Co(NO₃)₂·6H₂O and HReO₄. The following supports have been included in the study: γ -Al₂O₃ (Puralox SCCa-5/200 from Condea; treated with air at 773 K for 10 h), SiO₂ (PQ corp. CS-2133; treated with air at 773 K for 10 h), and TiO₂ (Degussa P25; treated with air at 973 K for 10 h, rutile). The catalysts were dried in air at 393 K for 3 h, before calcination in air at 573 K for 16 h. Before the experiments the catalysts were sieved to 53–90 μ m.

2.2. Temperature-programmed reduction

Temperature-programmed reduction (TPR) studies for both calcined and reduced catalyst were performed in a U-shaped tubular quartz reactor heated by an electrical furnace. For the TPR measurements of calcined catalysts, the reactor was loaded with 0.2 g of catalyst and heated at a rate of 10 K/min to 1203 K with a gas consisting of 7% H₂ in Ar. The gas flow rate was 30 ml/min. For the TPR experiments with reduced catalyst, 0.5 g of catalyst was loaded into the reactor. The catalyst was reduced in situ in a flow of hydrogen (30 ml/min), with temperature programming from ambient to 623 K at a rate of 1 K/min. The temperature was held at 623 K for 16 h before the temperature was reduced to ambient. The catalyst was flushed with Ar for 1 h and then heated at a rate of 10 K/min to 1203 K with a gas consisting of 7% H₂ in Ar (30 ml/min). The H₂ consumption was measured by analysis of the effluent gas with a thermal conductivity detector. Calibration was done by reduction of Ag₂O powder in the usual way.

2.3. H₂ chemisorption

H₂ adsorption isotherms were measured at 313 K in a standard volumetric glass apparatus (Micromeritics ASAP 2010) capable of achieving a vacuum of 10⁻⁵ Torr or better. The reactor was loaded with 0.2–0.5 g of catalyst. Before measurements the catalysts were reduced in flowing hydrogen with temperature programming from ambient to 623 K at a rate of 1 K/min. The temperature was kept at 623 K for 10 h. After reduction the samples were evacuated for 0.5 h at 603 K before they were cooled to 313 K [19], and the adsorption isotherm was measured between 10 and 510 Torr. After 30 min of pumping a second isotherm was measured to separate strongly and weakly held hydrogen. Only the total amount of hydrogen adsorbed is reported here. The amount of hydrogen chemisorbed was determined by extrapolation of the linear part of the isotherm to zero pressure. It is assumed, as done previously, that Re does not contribute to the amount of hydrogen chemisorbed when the dispersion is calculated [20] and that the adsorption stoichiometry is H:Co = 1.

2.4. Pulse oxidation

The extent of reduction was determined by pulse oxidation with O₂ of reduced samples at 673 K in the same apparatus as the TPR experiments. After reduction at 623 K for 10 h (heating rate from ambient to 623 K: 1 K/min), the sample was heated to 673 K in He and kept for 1 h to desorb any chemisorbed H₂. Calibrated pulses of O₂ were then added to the continuous He flow until no further consumption of O₂ was detected by the thermal conductivity detector located downstream of the reactor. The amount of O₂ consumed was calculated from known pulse volume, temperature, pressure, and the number of pulses reacting with the

catalyst. The extent of reduction was calculated assuming stoichiometric reoxidation of metallic Co to Co₃O₄.

2.5. BET surface area

BET surface area measurements were performed in a Carlo Erba Multisampler 1900 apparatus by N₂ adsorption. The samples were evacuated and dried at 423 K before analysis.

2.6. Pore size measurements

Pore diameter, pore size distribution, and pore volume for Al₂O₃- and SiO₂-supported catalysts were determined by N₂ adsorption in a Micromeritics Tristar 3000 instrument. The samples were degassed and dried at 373 K before measurement. Pore diameter, pore size distribution, and pore volume measurements for the TiO₂-supported catalysts were performed with a Carlo Erba Porosimeter 2000 by Hg intrusion. Each sample was evacuated and dried at 423 K before analysis.

2.7. X-Ray diffraction

X-ray diffraction studies were performed in a Philips PW 1710 spectrometer using monochromatic Cu-K_α radiation. The measurements were made on calcined catalysts, and average Co₃O₄ particle sizes were calculated from the most intense Co₃O₄ line, with the use of the Scherrer formula [21].

We obtained the Co₃O₄ particle size by assuming spherical particles and correcting the crystallite thickness obtained from the Scherrer formula by a factor of 4/3 [21]. To compare Co₃O₄ particle sizes calculated from XRD with the dispersion obtained from chemisorption, the Co₃O₄ particle sizes were converted to the corresponding Co particle sizes according to the relative molar volumes of metallic cobalt and Co₃O₄ [2]. The resulting conversion factor for the diameter d of a given Co₃O₄ particle being reduced to metallic cobalt is

$$d(\text{Co}^0) = 0.75d(\text{Co}_3\text{O}_4). \quad (1)$$

Dispersion can then be calculated from average metal particle sizes, assuming spherical, uniform cobalt particles with site density of 14.6 atoms/nm², using the formula [3]

$$D = \frac{96}{d}, \quad (2)$$

where D is the dispersion (%) and d (nm) is the particle diameter.

2.8. Activity and selectivity measurements

The experiments were carried out in a stainless-steel fixed-bed reactor (i.d. 10 mm). Catalyst (1–2 g, particle size 53–90 μm) was diluted with inert SiC (75–150 μm) in a

weight ratio of 0.2–0.5 (depending on the catalyst activity) to minimize temperature gradients. An aluminum jacket was placed outside the reactor to further reduce possible temperature gradients. These conditions also ensure the absence of mass transfer limitations on the rate of CO conversion [22]. The catalysts were reduced in flowing hydrogen at atmospheric pressure and a temperature of 623 K for 16 h (heating rate from ambient to 623 K: 1 K/min). After reduction the temperature was reduced to 443 K and the reactor was purged with helium for 1 h, before the pressure was increased to 20 bar. Synthesis gas (200 ml/min) with a H₂/CO ratio of 2.1 (and about 3% N₂) was then switched to the reactor, and the temperature was slowly increased to 483 K. A slow startup procedure was adapted to maintain catalyst activity and to avoid runaway. The first 5 h are not reported because this was the time it took to reach steady-state conditions in terms of composition and temperature. On-line GC samples were taken at regular intervals and analyzed for H₂, N₂, CO, CO₂, and C₁₊ hydrocarbons. A HP 5890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used. The space velocity was adjusted to give a conversion about 40–45%. We added steam by feeding water (distilled) with a liquid flow controller into a vaporizer kept at 648 K. The steam generated was mixed with synthesis gas just prior to the reactor inlet. The water was degassed with helium at least 16 h before use.

The C₅₊ selectivity was calculated by difference from the total mass balance and selectivity for C₁–C₄ components. The activity is reported as the hydrocarbon formation rate (r , g_{HC}/(g_{cat} h)). The calculation is based on the assumption of a pseudo-first-order reaction in a plug flow reactor [23].

3. Results and discussion

3.1. Catalyst characterization

TPR curves for all of the catalysts before and after reduction at 623 K are included as Figs. 1–3 to ease the comparison with other catalysts. It is usually assumed that the peaks at 640 and 670 K for Co/Al₂O₃ and CoRe/Al₂O₃ (Fig. 1) are due to the reduction of large crystalline Co₃O₄ particles and that the peaks above 700 K are due to the reduction of highly dispersed cobalt oxide phases interacting with the support [24,25]. According to Lapidus et al. [26] and van Steen et al. [27] the nitrate precursor is completely thermally decomposed at 573 K (which is the temperature of calcination). Arnoldy and Moulijn [28] found that nitrate can only be completely removed by calcination at ca. 650 K, and Hoff et al. [29] showed that a calcination temperature of about 673 K is necessary to achieve an almost complete decomposition of cobalt nitrate. With this in mind and taking earlier TPR results on Co/Al₂O₃ and CoRe/Al₂O₃ catalysts [2] into account, we suggest that the peaks at 530 and 590 K correspond to reductive decomposition of Co-nitrate remaining

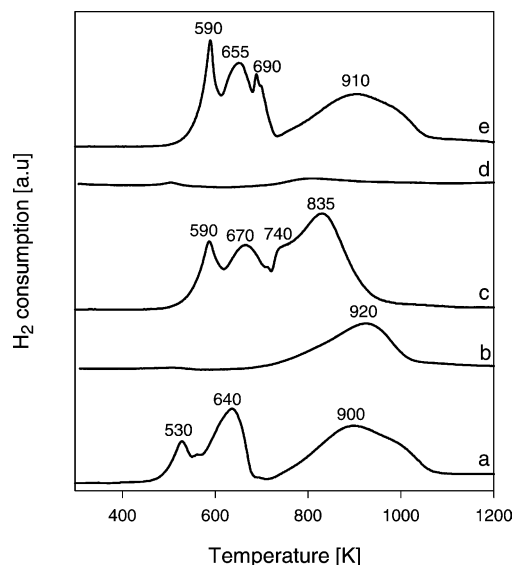


Fig. 1. TPR of 12% Co/Al₂O₃ after calcination (a), 12% Co/Al₂O₃ after reduction (623 K, 16 h) (b), 12% Co–0.5% Re/Al₂O₃ after calcination (c), 12% Co–0.5% Re/Al₂O₃ after reduction (623 K, 16 h) (d), and 12% Co/Al₂O₃ after calcination using a closed reactor configuration, i.e., no air supplied (623 K, 16 h) (e).

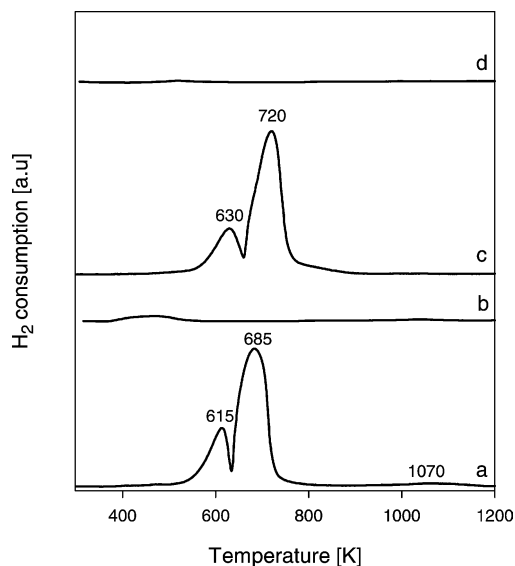


Fig. 2. TPR of 12% Co/SiO₂ after calcination (a), 12% Co/SiO₂ after reduction (623 K, 16 h) (b), 12% Co–0.5% Re/SiO₂ after calcination (c), and 12% Co–0.5% Re/SiO₂ after reduction (623 K, 16 h) (d).

after calcination. This is further confirmed by curve e in Fig. 1, which shows the TPR curve for Co/Al₂O₃ calcined without air supplied. In this way the concentration of NO_x surrounding the catalyst is higher compared with normal calcination conditions. As indicated by Fig. 1e, the higher NO_x concentration during calcination results in more residual nitrate on the catalyst. The temperature for appearance of the Co-nitrate peak depends upon the degree of interaction with the support, and the stronger interaction on the Al₂O₃ requires a higher temperature for decomposition of

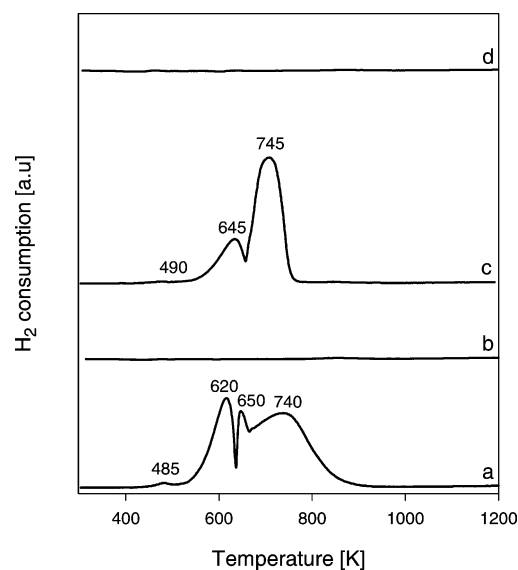


Fig. 3. TPR of 12% Co/TiO₂ after calcination (a), 12% Co/TiO₂ after reduction (623 K, 16 h) (b), 12% Co–0.5% Re/TiO₂ after calcination (c), and 12% Co–0.5% Re/TiO₂ after reduction (623 K, 16 h) (d).

Co-nitrate. Addition of rhenium causes the high-temperature peak to shift to a lower temperature as expected, and the shoulder on the high-temperature peak is likely due to cobalt species with varying degrees of support interaction that depend on the cluster size [30]. TPR of reduced Co/Al₂O₃ and CoRe/Al₂O₃ shows that a large part of the high-temperature peak remains after reduction of the unpromoted catalyst, but this high-temperature peak is just about absent after reduction of the Re-promoted catalyst (Figs. 1b and d). Because of the strong interaction between cobalt and the support in Co/Al₂O₃, a large part of the cobalt oxide is not reduced. However, with the addition of rhenium to the Co/Al₂O₃ catalyst, the reduction of cobalt is promoted, and a larger part of the cobalt is reduced under both TPR conditions and normal reduction conditions (623 K, 16 h). From the TPR results, for the SiO₂-supported and TiO₂-supported catalysts, there is no obvious effect on the reducibility created by the addition of rhenium.

The TPR profile of Co supported on SiO₂ contains mainly two peaks corresponding to a two-step reduction (Co³⁺ → Co²⁺ → Co⁰) of large crystalline Co₃O₄ particles. The unpromoted catalyst also contains a very small high-temperature peak. Two hypotheses have been proposed to explain the high-temperature peak [31]. The peak may be due to the presence of cobalt silicate or alternatively to reduction of a fraction of cobalt that is contained in the inner cavities of the silica support. The high-temperature peak observed for Co/SiO₂ has disappeared after promotion with rhenium. This effect of the Re promotion could indicate that the high-temperature peak is linked with a chemical effect, that is, a form of cobalt oxide stabilized by the support, like cobalt silicate or a similar species. TPR profiles of the reduced Co/SiO₂ and CoRe/SiO₂ catalysts indicate

Table 1
Characterization results: dispersion, particle size and extent of reduction

Catalyst	Dispersion ^a (H ₂ -ads.) [%]	Particle size ^b (H ₂ -ads.) [nm]	Particle size ^c (XRD) [nm]	Dispersion ^d (XRD) [%]	Extent of reduction ^{e,f} [%]
Co/Al ₂ O ₃	6.3	15.2	10.9	8.8	53
CoRe/Al ₂ O ₃	10.2	9.4	11.5	8.3	61
Co/SiO ₂	5.3	18.1	19.6	4.9	65
CoRe/SiO ₂	5.8	16.4	15.8	6.1	66
Co/TiO ₂	2.3	41.7	38.7	2.5	69
CoRe/TiO ₂	2.4	40.0	56.9	1.7	71

^a Cobalt metal dispersion from H₂ chemisorption at 313 K, assuming adsorption on Co atoms only.

^b Cobalt metal particle size calculated from H₂ chemisorption using $d(\text{Co}) = 96/D$.

^c Cobalt metal particle size calculated from XRD of calcined catalyst, using $d(\text{Co}) = 0.75d(\text{Co}_3\text{O}_4)$.

^d Cobalt metal dispersion calculated from XRD data, using the relation $D = 96/d(\text{Co})$.

^e Extent of reduction calculated from pulse oxidation with O₂ at 673 K.

^f The uncertainty is calculated to be $\pm 1\%$ based on standard deviation from multiple experiments.

that mainly all cobalt oxide reduced under TPR conditions is completely reduced after 16 h at 623 K (Figs. 2b and d).

The TPR of calcined, unreduced Co/TiO₂ (Fig. 3a) shows four peaks, and the TPR of calcined, unreduced CoRe/TiO₂ (Fig. 3c) shows three peaks. The low-temperature peaks at 485 and 490 K correspond to reductive decomposition of Co-nitrate remaining after calcination [32]. Both low-temperature peaks are relatively small compared with the other peaks, and, bearing in mind that decomposition of 1 mol of Co-nitrate requires 3 mol of H₂, only minor amounts of Co-nitrate remained after calcination. For calcination temperatures above 673 K no residual Co-nitrate is observed after calcination for TiO₂-supported catalysts [31,33]. The lower temperature observed for the decomposition of Co-nitrate on TiO₂-supported catalysts confirms a lower degree of interaction between Co-nitrate and the support compared with Al₂O₃-supported catalysts. The peaks at 620, 650, and 740 K in Fig. 3a and the peaks at 645 and 725 K in Fig. 3c are due to the reduction of Co₃O₄ to Co⁰. The broad peak in Fig. 3a is presumably due to the reduction of species for which there exists a range of degrees of interaction of the cobalt oxide with the support [24,34]. Promoting with rhenium shifts the broad peak at high temperature to a narrower peak at lower temperature. Re is a classical reduction promoter. Because Re is reduced at 690 K, only the reduction of the high-temperature peak is affected by Re, probably by spillover of hydrogen from Re, making the reduction of Co in interaction with the support easier [25]. Like the SiO₂-supported catalysts, all of the cobalt oxide reduced at TPR conditions for Co/TiO₂ and CoRe/TiO₂ is completely reduced after 16 h at 623 K (Figs. 3b and d).

Catalyst dispersion, particle size, and extent of reduction for all of the catalysts are shown in Table 1. As expected, the extent of reduction shows that Re increases the degree of reduction of Co supported on Al₂O₃ from 53 to 61%. For the SiO₂- and TiO₂-supported catalysts the results show no effect of Re on the degree of reduction. The differences given in Table 1 for the catalysts supported on SiO₂ and TiO₂ are clearly within the experimental uncertainty.

The chemisorption results given in Table 1 have been calculated with the assumptions that the adsorption stoichiometry is H:Co = 1 and that Re does not contribute to the amount of hydrogen chemisorbed, in agreement with previous experimental results and theoretical calculations [20].

As shown in Table 1, volumetric chemisorption gives a higher dispersion for the rhenium-promoted Co/Al₂O₃ catalyst than for the unpromoted one. According to previous studies, this is due to rhenium promoting the reduction of highly dispersed cobalt phases [2]. The same promoting effect of Re is not observed from the XRD measurements. In this case the observed dispersion is slightly lower for CoRe/Al₂O₃ compared with Co/Al₂O₃. The main reasons for this are probably that XRD does not measure the smallest particles [35], the highly dispersed phases present lack crystallinity, and the XRD measurements were done on oxide catalysts instead of on reduced catalysts as in volumetric chemisorption. For the Al₂O₃-supported Co catalyst, the dispersion measured by chemisorption increases by two-thirds as a result of the addition of Re, whereas the effect of adding rhenium to the Co/SiO₂ catalyst is much less pronounced. On TiO₂ the addition of Re leads to no change in the hydrogen chemisorption, whereas the XRD measurements indicate that Re leads to slightly larger Co particles and lower dispersion. In general the particle sizes calculated from XRD are in good agreement with the particle sizes calculated from H₂ chemisorption.

The BET surface areas, pore diameter, pore volumes, and pore size distribution are given in Table 2. There are very small differences between Re-promoted and unpromoted catalysts, but the pore size distribution (figures not shown in this paper) shows that Re-promoted Co catalysts supported on SiO₂ and TiO₂ have a slightly higher fraction of the largest pores than their unpromoted counterparts. The Al₂O₃-supported catalysts have the smallest pores (~ 67 Å), the narrowest pore size distribution, the smallest pore volume (~ 0.35 cm³/g), and a surface area (160 m²/g) between those of SiO₂ and TiO₂. The SiO₂-supported catalysts have a slightly higher pore size (~ 115 Å), a broader pore size

Table 2
Characterization results: pore diameter, pore volume and surface area

Catalyst	Average pore diameter [nm]	Pore size distribution [nm]	Pore volume [cm ³ /g]	Surface area ^c [m ² /g]
Co/Al ₂ O ₃	6.7 ^a	5–9 ^a	0.34 ^a	161
CoRe/Al ₂ O ₃	6.8 ^a	5–9 ^a	0.36 ^a	155
Co/SiO ₂	11 ^a	9–15 ^a	1.0 ^a	297
CoRe/SiO ₂	12 ^a	9–16 ^a	1.1 ^a	302
Co/TiO ₂	770 ^b	100–8000 ^b	0.77 ^b	8
CoRe/TiO ₂	790 ^b	100–8000 ^b	0.90 ^b	12

^a Calculated from N₂ adsorption measurements.

^b Calculated from Hg porosimetry measurements.

^c BET surface area calculated from N₂ adsorption measurements.

Table 3
Activity and selectivity at 40–45% CO conversion prior to any water addition, and turnover frequencies (TOF) at initial conditions. H₂/CO = 2.1, P_{Tot} = 20 bar, T = 483 K

Catalyst	GHSV [ml/(g _{cat} h)]	CO conversion [%]	Hydrocarbon formation rate [g _{HC} /(g _{cat} h)]	Selectivity ^a [%]		TOF ^b [s ⁻¹]
				CH ₄	C ₅₊	
Co/Al ₂ O ₃	2982	42.6	0.25	9.7	80.2	0.052
CoRe/Al ₂ O ₃	5960	42.8	0.42	8.8	80.8	0.052
Co/SiO ₂	3060	40.4	0.24	9.1	81.7	0.054
CoRe/SiO ₂	4166	40.3	0.33	8.7	83.4	0.056
Co/TiO ₂	1885	39.8	0.14	10.2	81.6	0.053
CoRe/TiO ₂	3595	42.6	0.30	8.9	84.8	0.12

^a The uncertainty ($\pm 2\sigma$) is estimated to be $\pm 0.4\%$ based on repeated measurements.

^b The TOFs are calculated from initial GHSV and CO conversion.

distribution, and a pore volume that is three times larger (~ 1.0 cm³/g) compared with the Al₂O₃-supported catalysts. The SiO₂-supported catalysts also have the largest surface area. The pore sizes for the TiO₂-supported catalysts (~ 0.78 μ m) are very large compared with the other catalysts, and the pore size distribution is remarkably broader, but the pore volume (0.85 cm³/g) does not differ from that of the other catalysts in the same way as the pore sizes. The surface area (~ 10 m²/g) is very low for the TiO₂-supported catalysts compared with the other catalysts.

3.2. Effect of water on the activity for Co-supported catalysts

We studied the effect of water on the activity and selectivity of cobalt Fischer–Tropsch catalysts by changing the GHSV (and thereby the conversion) and by co-feeding different amounts of water (inlet $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 0.38$ and $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 0.76$) to the reactor at constant conversion (40–45%). The selectivity and activity of the different catalyst were compared at the same conversion level rather than at constant GHSV. Previous results have shown that the selectivities strongly depend upon conversion [1]. After water co-feeding the conditions were adjusted to those used before water was added so as to compare directly the deactivation of the different catalysts. The experiments were performed for Co and CoRe supported on Al₂O₃, SiO₂, and TiO₂. In Table 3 the hydrocarbon formation rate, the C₅₊ selectiv-

ities, and the CH₄ selectivities at 40–45% conversion and under dry conditions are given together with the turnover frequencies at initial conditions. The main trend is that the activity depends on the support and on the cobalt dispersion. Re-promoted catalysts are more active (per gram of catalyst) than their unpromoted counterparts. This has earlier been reported to be caused by increased reducibility and increased number of surface-exposed Co atoms for promoted catalysts [36]. CoRe/Al₂O₃ catalyst is the most active catalyst, and Co/TiO₂ shows the lowest hydrocarbon formation rate. For all of the other samples the hydrocarbon formation rates do not differ very much.

Table 4 shows the hydrocarbon formation rate, the C₅₊ selectivities, and the CH₄ selectivities shortly after water addition. The addition of water causes some deactivation, and the hydrocarbon formation rate is therefore followed as a function of time on stream. Fig. 4 shows the rate of formation of hydrocarbons (g_{HC}/(g_{cat} h)) as a function of time on stream when the GHSV is reduced (to adjust the conversion to 40–45%) and when different amounts of water are added to the feed for Co and CoRe catalysts supported on Al₂O₃, SiO₂, and TiO₂. The formation rates measured after water was removed from the feed are also included in the figure. As indicated by Fig. 4A, a small increase in the rate is observed when GHSV is reduced for both CoRe and Co supported on Al₂O₃. Part of the increase may be due to an increase in temperature inside the reactor when the conversion is increased, although such an increase is not easily

Table 4

Conversion, activity and selectivity shortly after addition of about 20% water at 40–45% conversion. $H_2/CO = 2.1$, $P_{Tot} = 20$ bar, $T = 483$ K

Catalyst	CO conversion [%]	Hydrocarbon formation rate [g _{H_C} /(g _{cat} h)]	Selectivity ^a [%]	
			CH ₄	C ₅₊
Co/Al ₂ O ₃	39.5	0.23	6.7	83.0
CoRe/Al ₂ O ₃	35.1	0.34	6.5	83.8
Co/SiO ₂	46.0	0.28	5.4	87.5
CoRe/SiO ₂	46.4	0.38	5.1	88.6
Co/TiO ₂	47.8	0.18	5.2	90.1
CoRe/TiO ₂	53.1	0.37	4.7	91.4

^a The uncertainty ($\pm 2\sigma$) is estimated to be $\pm 0.4\%$ based on repeated measurements.

observed by the thermocouple. In accordance with previous results on Al₂O₃-supported Co catalysts, the reaction rate decreases with time on stream and the rate of deactivation increases when water is added [1–3,5,6]. Increasing the amount of co-fed water also increases the rate of deactivation. For both Co/Al₂O₃ and CoRe/Al₂O₃ the activity seems to return to about the level observed before the second water period; that is, some of the deactivation caused by the water addition is reversible. Similar behavior has been observed for Pt-supported Co/Al₂O₃ catalyst [4]. The deactivation of the Al₂O₃-supported Co catalysts in the presence of water is probably mostly due to reoxidation of metallic cobalt [3,5,37]. The extent of reoxidation depends on the partial pressure of water and the P_{H_2O}/P_{H_2} ratio in the feed.

The loss in activity and the rate of deactivation are greater for the Re-promoted catalyst compared with the unpromoted catalyst. Adding about 20% water (inlet $P_{H_2O}/P_{H_2} = 0.38$) caused deactivation of the catalyst over a period of 20 h by 28 and 37% of the initial activity for Co/Al₂O₃ and CoRe/Al₂O₃, respectively. The rate [g_{H_C}/(g_{cat} h)] for the CoRe/Al₂O₃ is higher than for Co/Al₂O₃, in accordance with the dispersion measurements given in Table 1. The higher dispersion observed for the CoRe/Al₂O₃ catalyst may also be the reason for the increased tendency to oxidize. As Fig. 1 indicates, Re promotes the reduction of highly dispersed cobalt oxide interacting with the support, thereby increasing the degree of reduction. Re might have the same effect on the reverse reaction, increasing the rate and the degree of oxidation due to water. Water may also influence the metal-support interactions. The rate of deactivation decreases with time for both catalysts, indicating that the rate of deactivation also depends on the remaining activity in addition to the partial pressure of water.

Fig. 4B clearly shows that with an increase in the conversion (decreasing GHSV), the rate increases for both Re-promoted and unpromoted Co supported on SiO₂. This behavior suggests that one of the reaction products increases the rate of reaction. The catalysts deactivate faster as the conversion is increased, indicating that one of the products, in addition to increasing the reaction rate, also leads to deactivation. Adding about 20% water increases the rate for both catalysts even more, and they start to deactivate rather quickly, confirming that water is the product responsible for

the increased reaction rate and the increased rate of deactivation at higher conversions. The rate of deactivation decreases with time, as observed for the Al₂O₃-supported catalysts. Adding more water does not increase the activity further; instead the catalyst deactivates even more. This indicates that the activity is passing through a maximum depending on the partial pressure of water and the inlet P_{H_2O}/P_{H_2} ratio. After water is removed from the feed, the activity decreases at first before some of the activity lost during water addition is recovered. The activity increase and the deactivation presented in Fig. 4B are consistent with the results obtained by Krishnamoorthy et al. [7]. The recovery of some of the activity after added water was removed from the feed is in contrast to what has been observed by others [8]. It has previously been reported that the deactivation occurring at high conversions or at high water partial pressures is irreversible; the catalyst does not regain any activity after re-reduction, showing that the deactivation is not due to oxidation of cobalt [10]. Support collapse and the formation of cobalt silicates [10] have been proposed as an explanation for the observed deactivation. Although our results show some recovery of the activity, the main trend is permanent deactivation, in general agreement with the suggestions made by Huber et al. [10].

Under dry conditions the reaction rate for CoRe/SiO₂ is slightly higher than the corresponding rate for Co/SiO₂, as expected from the dispersion data given in Table 1. Re does not increase the reducibility or the dispersion for Co/SiO₂ to any large extent. However, the difference in reaction rate at a conversion of $\sim 45\%$ is larger than can be ascribed to the difference in dispersion, and we propose that this can be ascribed to different surface coverages of reactive intermediates, leading to products for the promoted and unpromoted catalysts, as previously observed in SSITKA experiments at lower pressure [36]. On SiO₂ there is no observable difference in the rate of deactivation between the Re-promoted and the unpromoted catalyst.

As shown in Fig. 4C the rate increases with increasing conversion for Co and CoRe supported on TiO₂. The rate also increases with the addition of 20% water to the feed, which is similar to what was observed for the SiO₂-supported catalyst. However, when TiO₂ is used as the support, there is almost no deactivation, even at high conversion or when water is added. As for the SiO₂-supported catalysts,

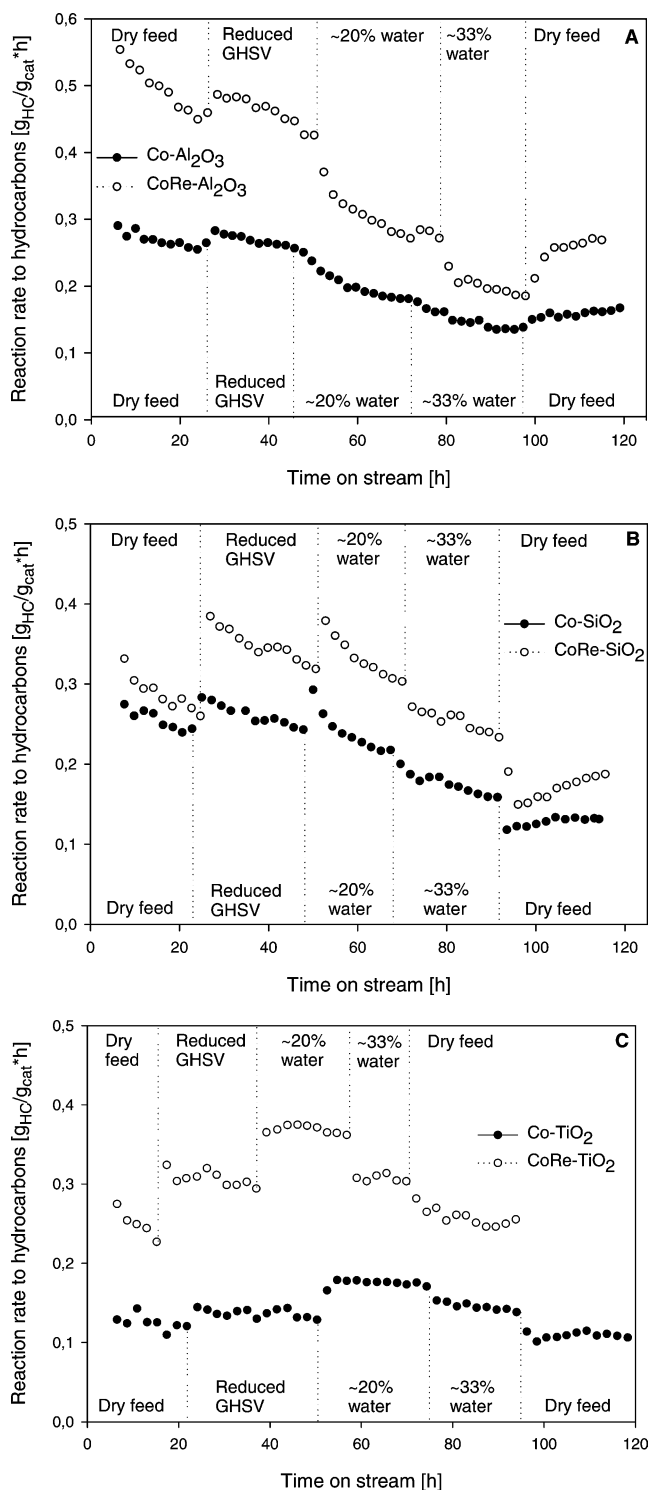


Fig. 4. Observed reaction rate for formation of hydrocarbons as a function of time on stream 5 h after start-up for Co (●) and CoRe (○) catalysts supported on Al_2O_3 (A), SiO_2 (B), and TiO_2 (C). $\text{H}_2/\text{CO} = 2.1$, $P_{\text{Tot}} = 20$ bar, $T = 483$ K.

the rate is lower at 33% water addition than at 20% water addition. Only a small deactivation is observed. For both catalysts the rate after removal of the water from the feed is only 15% lower than the rate observed before water was added.

The positive effect of water on the activity observed for the TiO_2 -supported Co catalysts is in agreement with earlier results [11–13].

CoRe/TiO_2 and Co/TiO_2 behave in the same way, except that the Re-promoted catalyst is twice as active [$\text{g}_{\text{HC}}/(\text{g}_{\text{cat}} \text{h})$] as the unpromoted catalyst. The difference in the rate of hydrocarbon formed between the two catalysts is higher at $\sim 45\%$ conversion and wet conditions than at initial conditions similar to what was observed for the SiO_2 -supported catalysts. At higher conversions more water is being produced and the water enhances the rate for both catalysts in the same way as when external water is being added.

The large difference in activity between Co/TiO_2 and CoRe/TiO_2 has been observed by others [12,34,38,39] and has been associated with different dispersions. Iglesia et al. [12] found that Re acts as a structural promoter, leading to higher dispersion on TiO_2 , without influencing FTS turnover rates. This effect is observed only when the cobalt nitrate precursors are exposed to a high temperature in an oxidizing environment before reduction. Oukaci et al. [38] have explained the observed enhancement in activity by Re promotion as being due to initial reduction of Co at lower temperatures, which in turn increases the dispersion of the reduced cobalt. Li et al. [34] found that the enhanced activity is due to the increased reducibility of the catalyst, and Mauldin et al. [39] explained the large difference in activity by better cobalt oxide dispersion and reduction of well-dispersed cobalt oxide at lower temperatures with Re as a promoter.

The dispersion for Co/TiO_2 and for CoRe/TiO_2 as measured by chemisorption (Table 1) is 2.3 and 2.4, respectively. Therefore the dispersion cannot explain the observed enhancement in activity. The same effect has been seen for Ru-promoted Co/TiO_2 catalyst. Iglesia et al. [40] found that promotion with very small amounts of Ru increases the FTS turnover rates on Co/TiO_2 without an apparent change in cobalt dispersion. This effect has been explained by a bimetallic effect created during the calcination treatment. An intimate contact between Co and Ru occurs during calcinations; this lowers the Co oxide reduction temperature and inhibits carbon deposition on bimetallic CoRu catalysts. Others have observed activity increased by promotion with Ru, and this has been explained as being due to increased dispersion [34,38].

The dispersions given in Table 1 based on H_2 chemisorption for the TiO_2 -supported catalysts could be erroneous. For titania-supported noble metal catalysts, strong metal-support interactions (SMSI) are observed when the reduction temperature is above 573 K [41]. Materials with SMSI exhibit a diminished hydrogen adsorption capacity without a significant enlargement of particles due to migration and bonding of a suboxide (TiO_x), induced by reduction, from the support to the metal particles [42]. All of the catalysts studied in this work were reduced at 623 K before the chemisorption measurements and the kinetic studies, indicating that there is a possibility that SMSI exists for the titania-supported

catalysts. This means that the dispersions measured by volumetric chemisorption for the TiO₂-supported catalysts are probably too small. This is especially the case for the Re-promoted catalysts, where Re may activate the hydrogen for reduction of the support.

As a consequence of higher activity but the same dispersion for CoRe/TiO₂ compared with Co/TiO₂, the turnover frequency for CoRe/TiO₂ given in Table 3 is higher compared with that of the other catalysts. This effect was observed earlier for TiO₂-supported group VIII metals, even after a low temperature reduction (573 K) [42]. A proposed explanation for this is that the support is partly reduced during reduction due to SMSI and at low-temperature reduction, resulting in the formation of TiO_x species. During low-temperature reduction, these species do not have enough mobility to achieve a significant transport over the metal, but they do have a promoting effect on the CO/H₂ reaction. The promoting effect of TiO_x has been explained in terms of a higher rate for CO dissociation [42], which in turn will result in a higher TOF.

3.3. Effect of water on C₅₊ and CH₄ selectivity

The reaction network in the Fischer–Tropsch synthesis is very complex, and the selectivities depend on the reaction rate for many reactions. A simplified representation of the reaction network is given in Fig. 5. A *C_n species on the surface can react in three ways: termination by hydrogenation to a paraffin, termination by hydrogen abstraction to an α-olefin, or propagation to higher hydrocarbons. A primary α-olefin can react in two ways: it can either be secondarily hydrogenated to a paraffin or readsorb with subsequent chain initiation. Because of several reaction possibilities it is evident that a reduction in secondary hydrogenation does not necessarily result in an increase in the olefin selectivity, because of the other reactions that have to be taken into account. In the two following sections the selectivities are discussed in terms of the reaction network presented in Fig. 5.

Fig. 6 shows the selectivity of C₅₊ and CH₄ as a function of the conversion of CO under dry conditions, at different water additions, and after removal of the water for all of the catalysts involved in this study. For the Al₂O₃-supported catalysts (Figs. 6A and B) the C₅₊ selectivity increases and the CH₄ selectivity decreases as the CO conversion is in-

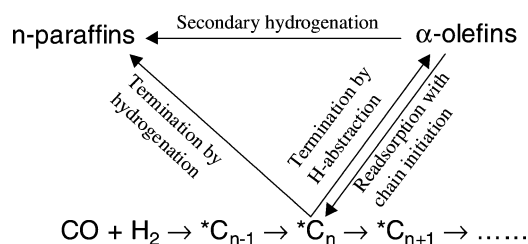


Fig. 5. Simplified reaction network of the Fischer–Tropsch synthesis. C_{n-1}, C_n, and C_{n+1} represent the growing chain on the catalyst surface.

creased under dry conditions, as has been observed previously [1,43]. Co-feeding water to the reactor inlet increases the C₅₊ selectivity and decreases the CH₄ selectivity further, and the effect is larger at higher partial pressures of water. At some point the effect of adding more water is not that evident. After removal of water for the Co/Al₂O₃ catalyst, the CH₄ selectivity is 1% higher than before water addition and the C₅₊ selectivity is 4% lower than before water addition. For the CoRe/Al₂O₃ catalyst the C₅₊ selectivity and the CH₄ selectivity return to the level observed before the water addition.

For the SiO₂-supported catalysts (Figs. 6C and D) the C₅₊ selectivity increases and the CH₄ selectivity decreases as the CO conversion is increased under dry conditions. As observed previously, the C₅₊ selectivity is further increased when water is added [7]. When the partial pressure of water is rather high, the effect of adding more water is not very clear, but there is still a small positive effect. In agreement with the increase in C₅₊ selectivity, the CH₄ selectivity decreases, as water is co-fed. For the Co/SiO₂ catalyst the C₅₊ selectivity returns to the same value as before water addition, but for the CoRe/SiO₂ catalyst the C₅₊ selectivity is a few percent lower compared with the selectivity observed before water addition. The effect of increasing the conversion or adding water is larger for the SiO₂-supported catalysts than for the Al₂O₃-supported catalysts. The CoRe/SiO₂ catalyst achieves higher C₅₊ selectivity than the Co/SiO₂ catalyst (Tables 3 and 4).

The same effect is observed for the TiO₂-supported catalysts as for the Al₂O₃- and SiO₂-supported catalysts (Figs. 6E and F). The C₅₊ selectivity is increased and the CH₄ selectivity is decreased as the conversion is increased or water is added. However, in contrast to the Al₂O₃- and SiO₂-supported catalysts, the C₅₊ selectivity is a few percent higher after water addition (after the removal of water from the feed gas) than before water addition. The TiO₂-supported catalysts achieve the highest C₅₊ selectivity and the lowest CH₄ selectivity of the catalysts tested. Furthermore, the effect of increasing the conversion or adding water is greatest for the TiO₂-supported catalysts. The smaller increase in C₅₊ selectivity for the Al₂O₃-supported catalysts may be due to the fact that small cobalt particles on alumina can easily be reoxidized by water under the conditions of the Fischer–Tropsch synthesis. This affects the density of sites available for olefin readsorption and consequently the C₅₊ selectivity.

As for the SiO₂-supported catalysts, the Re-promoted Co/TiO₂ catalyst achieves higher C₅₊ selectivity than the unpromoted one (Tables 3 and 4). Bertole et al. [44] have recently claimed, based on SSITKA experiments, that Re does not affect Co site activity or selectivity. Jacobs et al. [45] have concluded from CSTR experiments that the CH₄ and C₅₊ selectivity is about the same for Re-promoted and unpromoted Co/Al₂O₃ catalyst. A positive effect of Re has previously been presented for low-surface and high-surface Al₂O₃ support [46]. This ef-

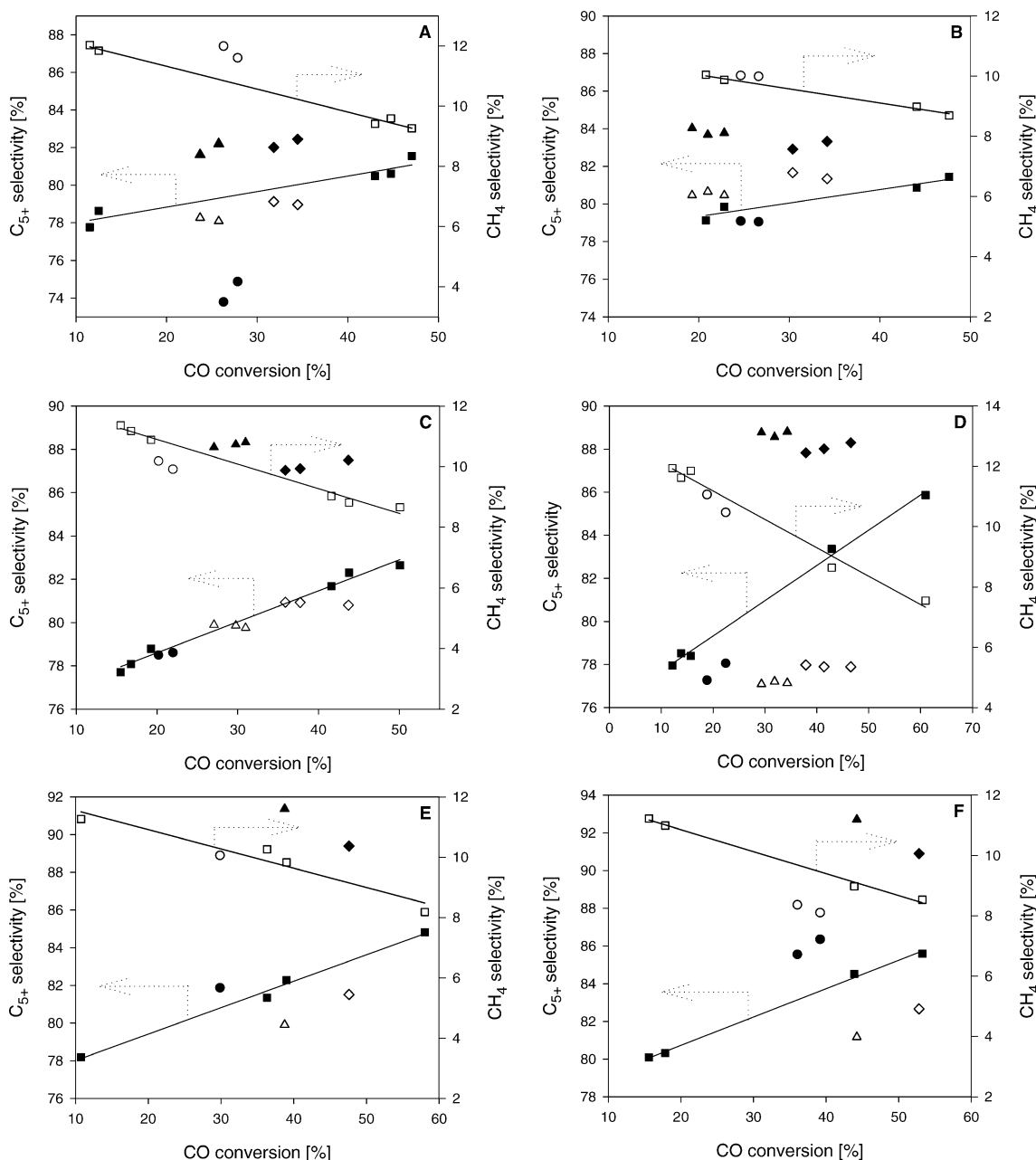


Fig. 6. C₅₊ selectivity (filled symbols) and CH₄ selectivity (open symbols) as a function of CO conversion at different conditions for Co/Al₂O₃ (A), CoRe/Al₂O₃ (B), Co/SiO₂ (C), CoRe/SiO₂ (D), Co/TiO₂ (E), and CoRe/TiO₂ (F). Before water addition (■, □), ~20% water added (◆, ◇), ~33% water added (▲, △) and after water addition (●, ○).

fect could probably arise from differences in the active surface carbon intermediates [7,36,47], leading to products.

The observed increase in C₅₊ selectivity as the conversion is increased has been attributed to secondary reactions (Fig. 5) of primary olefins at higher residence times in the liquid-filled pores [43]. It has also been shown that water inhibits secondary hydrogenation of primary olefins [19], and this effect may contribute to increased C₅₊ selectivity, since more olefins are available for insertion and chain growth at increasing amounts of water in the reactor. The increase in C₅₊ selectivity is mainly coupled with the decrease in CH₄

selectivity (propagation of ^{*}C₁ preferred over hydrogenation of ^{*}C₁ to CH₄), but there is also an effect on the C₂–C₄ selectivity. For the Co/Al₂O₃ the increase in C₅₊ selectivity as water is added is a little bit smaller than the decrease in CH₄ selectivity, but for all of the other catalysts the increase in C₅₊ selectivity is somewhat larger than the decrease in CH₄ selectivity. For the Co/Al₂O₃ catalysts a decrease in C₅₊ selectivity is observed after the period of water addition. This increase is 3% larger than the increase in CH₄ selectivity. This indicates that it is not only the decrease in the selectivity of CH₄ that contributes to the observed changes in C₅₊ selectivity.

3.4. Effect of water on olefin and paraffin selectivities and olefin/paraffin ratios

The content of olefins and paraffins is changed as the conversion is changed or external water is added. The effect of CO conversion under dry conditions, at different levels of water addition, and after removal of water on the selectivity of C₃-olefin and paraffin is presented in Fig. 7 for Co/SiO₂. Table 5 contains the C₃ selectivity data for all of the other catalysts. The same trends are observed for the C₂ and C₄ selectivities as for the C₃ selectivities; thus the values are not given here. As highlighted in Fig. 7A, the propene selectivity for Co/SiO₂ decreases as the conversion is increased, but is almost unaffected by water addition. The same effect of increasing the conversion on the propene selectivity is observed for the TiO₂- and the Al₂O₃-supported catalysts. The propene selectivity is increased for the Al₂O₃-supported catalysts and slightly decreased for the TiO₂-supported catalysts by water addition (Table 5). The decrease in propene selectivity that occurs when the conversion is increased is also larger for the SiO₂- and TiO₂-supported catalysts. For the Co/SiO₂ catalyst the propane selectivity (Fig. 7B) increases slightly as the conversion is increased but decreases as external water is added. The other catalysts show the same behavior regarding the propane selectivity, but the de-

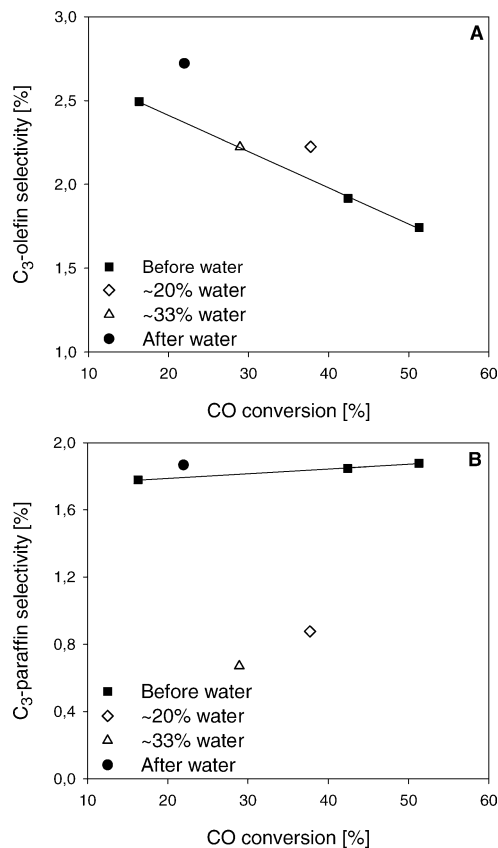


Fig. 7. C₃-olefin and paraffin selectivity as a function of conversion before, during and after water addition for 12% Co/SiO₂. H₂/CO = 2.1, P_{Tot} = 20 bar, T = 483 K.

crease in propane selectivity that occurs as water is added is most pronounced for the SiO₂- and TiO₂-supported catalysts (Table 5). The above results indicate that the degree of termination and the secondary reactions (Fig. 5) depend on the partial pressure of water and the residence time for the different supports. The rates are affected in various ways, depending on whether the CO conversion is increased or water is co-fed. The reason for the decreased olefin selectivity as the conversion is increased, in spite of higher water concentrations reducing the degree of secondary hydrogenation at higher conversions, is the higher extent of α -olefin readsorption at higher residence times [7]. The decrease in paraffin selectivity observed when water is added is due to a lower rate of secondary hydrogenation [19] and a lower rate of chain termination via hydrogen addition [12]. A comparison between the C₃-olefin and paraffin selectivities (Table 5) suggests increased readsorption at higher partial pressure of water. Another explanation could be that water influences the probability of chain growth (i.e., through inhibition of the termination reaction).

For all of the supports the C₃ selectivity is smaller for the Re-promoted catalysts than for the unpromoted ones (Table 5). The TiO₂-supported catalysts achieve the lowest C₃ selectivity, and the Al₂O₃-supported catalysts achieve the highest C₃ selectivity. For the C₅₊ selectivity the opposite trend is observed. For Co/Al₂O₃ the total C₃ selectivity is about unchanged as the conversion is increased but increases as water is added. The same trend is observed for the C₂ and C₄ selectivities, explaining why the increase in C₅₊ selectivity during water addition is smaller than the decrease in CH₄ selectivity for this catalyst. After water addition the total selectivity for C₂–C₄ hydrocarbons by the Co/Al₂O₃ catalyst increases even more, and is the main reason for the large decrease in C₅₊ after the water periods. For CoRe/Al₂O₃ only a small decrease in C₃ selectivity is observed as the conversion is increased or water is being added. For the TiO₂- and SiO₂-supported catalysts the total C₃ selectivity decreases with increasing conversion or with the addition of water (Table 5).

The olefin/paraffin ratios, as a function of time on stream for C₂–C₆ components for the Co/SiO₂ catalyst, are shown in Fig. 8. When the conversion is increased, the olefin/paraffin ratio is decreased for all catalysts, which implies more secondary reactions of olefins (Fig. 5) at higher residence times and changes in the termination mechanism. The olefin/paraffin ratio is increased when water is added to the feed, which points to a reduced secondary hydrogenation of primary olefins.

3.5. Comparison of different supports and the effect of water

Previous results for bulk Co catalyst showed that external water addition increases the CO conversion, increases the C₅₊ selectivity, and decreases the CH₄ selectivity [16]. It has been reported that water has no effect on the activity

Table 5

C₃-olefin selectivity, C₃-paraffin selectivity, total C₃ selectivity and C₃-olefin/paraffin ratio at different conditions and CO conversions. H₂/CO = 2.1, P_{Tot} = 20 bar, T = 483 K

Catalyst	Conditions and CO conversion [%]		C ₃ -Selectivity [%]			Olefin/paraffin ratio
			Olefin	Paraffin	Total	
Co/Al ₂ O ₃	Dry feed	11.5	3.1	1.0	4.1	3.1
	Dry feed	44.8	2.8	1.2	4.1	2.3
	~ 20% water	34.5	3.4	1.1	4.5	3.3
	~ 33% water	25.8	3.8	1.0	4.8	3.8
CoRe/Al ₂ O ₃	Dry feed	21.3	3.1	1.1	4.3	2.8
	Dry feed	47.6	2.8	1.3	4.1	2.3
	~ 20% water	28.7	3.2	0.9	4.1	3.5
	~ 33% water	19.3	3.2	0.8	4.0	4.0
Co/SiO ₂	Dry feed	16.7	2.5	1.8	4.3	1.4
	Dry feed	42.2	2.0	1.8	3.8	1.1
	~ 20% water	37.9	2.2	0.9	3.1	2.6
	~ 33% water	28.9	2.2	0.7	2.9	3.3
CoRe/SiO ₂	Dry feed	13.1	2.5	1.4	3.8	1.8
	Dry feed	41.2	1.9	1.3	3.2	1.4
	~ 20% water	39.5	1.9	0.7	2.6	2.7
	~ 33% water	31.0	1.9	0.6	2.5	3.3
Co/TiO ₂	Dry feed	11.1	2.7	1.4	4.1	2.0
	Dry feed	36.9	1.6	1.6	3.2	1.0
	~ 20% water	46.6	1.2	0.8	2.0	1.5
	~ 33% water	38.8	1.0	0.6	1.6	1.8
CoRe/TiO ₂	Dry feed	17.8	1.9	1.3	3.2	1.5
	Dry feed	43.9	1.1	1.3	2.5	0.8
	~ 20% water	52.8	0.9	0.7	1.6	1.4
	~ 33% water	44.4	0.8	0.4	1.3	1.8

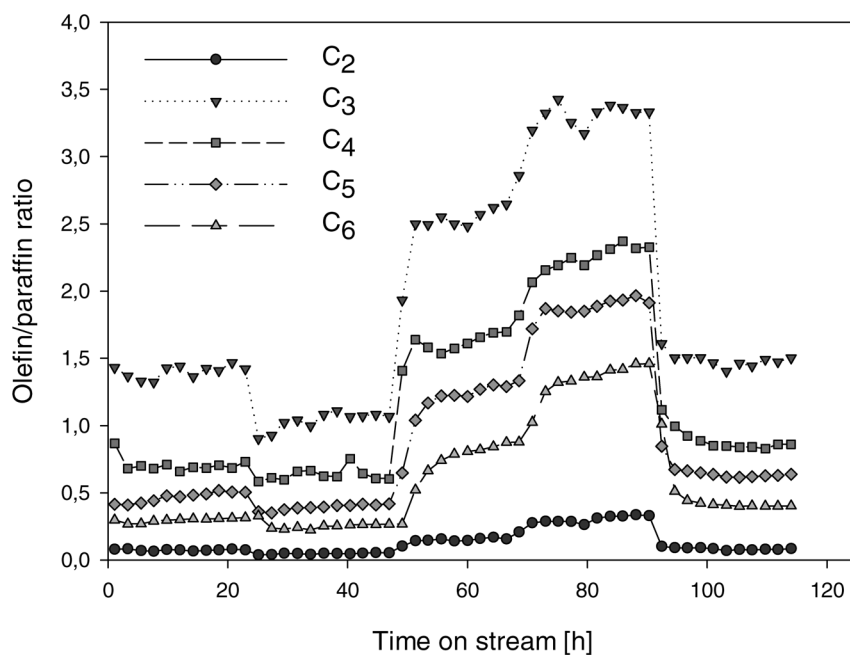


Fig. 8. Olefin/paraffin ratio as a function of time on stream for C₂–C₆ components for 12% Co/SiO₂. Step changes in olefin/paraffin ratio are due to increased GHSV at 23 h, ~ 20% water addition at 50 h, ~ 33% water addition at 70 h and back to the dry feed at 95 h. H₂/CO = 2.1, P_{Tot} = 20 bar, T = 483 K.

for a Co/ZrO₂/Aerosil catalyst, but the methane formation was suppressed and the chain growth was enhanced [18]. The behavior of the reaction rate in the presence of water for Co/SiO₂ catalysts has been found to be different for small-

pore silicas and large-pore silicas [12]. The effect of water on the C₅₊ selectivity is positive for all Co catalyst systems, but the water effect on the activity greatly depends upon the type of support used. The lower rate of secondary hydrogenation

and chain termination via hydrogen addition in the presence of water may indicate a lower availability of adsorbed hydrogen on the active Co surface. But this is not consistent with the activity increase observed upon water addition for some catalysts.

Several different theories for the effect of water have been proposed. Iglesia et al. [12] explained it by a separate intrapellet water phase, which facilitates CO and H₂ transport within the porous structure and increases the accessibility of isolated transport-limited regions within porous pellets. The pore size determines the partial pressure of water at which this phase will take form. Lately, Krishnamoorthy et al. [7] have ruled out the possibilities that new pathways are introduced by water, that water has a cleaning effect on the concentration of site-blocking unreactive intermediates, and that water removes significant CO transport restriction. Instead it was suggested that water influences the relative concentrations of active and inactive forms of carbon present at low concentrations on Co surfaces, but the mechanism still remains unclear. Another suggested explanation by Bertole et al. [11] is that a direct interaction between coadsorbed CO and water lowers the barrier to CO dissociation. The increased C₅₊ selectivity was associated with an increase in the active carbon coverage caused by an increase in CO reactivity without a parallel increase in the overall activity of surface carbon [11]. Recently, Bertole et al. [47] concluded from isotope transient kinetic studies under industrially relevant conditions that the rate of propagation to termination during chain growth in Fischer–Tropsch synthesis is strongly correlated with the steady-state amount of active carbon for all carbon number products, and that the dominant form of active carbon is monomeric. They also concluded that most of the effects of changes in CO and water partial pressures on the chain growth probability appear to arise via an indirect effect on the active carbon inventory.

The C₅₊ selectivity depends on the support pore structure and readsorption site density. The C₅₊ selectivity increases with increasing site density, and different pore structures influence the intrapellet residence times, which further affect the readsorption rates [43]. Differences in pore structures for Al₂O₃, SiO₂, and TiO₂, which can be attributable to a reduced olefin hydrogenation activity and enhanced readsorption activity, may be part of an explanation for the differences in C₅₊ selectivities and olefin/paraffin selectivities observed at equal conversions.

However, the results of this work also point to the influence of the particle size of cobalt on the C₅₊ selectivity. Alumina-supported catalysts with the smallest cobalt particles (Table 1) achieve the lowest C₅₊ selectivity, whereas titania-supported catalysts with the largest cobalt particles show the highest C₅₊ selectivity. Schanke et al. [46] found that Co supported on low-surface-area alumina with a high α -alumina content gives improved C₅₊ selectivities in FTS compared with high-surface-area alumina. The same effect of surface area can be seen from the present results; the C₅₊ selectivity for the low-surface-area titania catalysts is

prominent compared with the C₅₊ selectivity for the high-surface-area alumina catalysts, which again can be associated with larger Co particle sizes on low-surface-area titania compared with high-surface-area alumina. The size of the Co particles seems to depend on the pore size of the support. Supports with large pores (like TiO₂) exhibit larger Co particles than supports with smaller pores (like Al₂O₃). This is also in accordance with the slightly larger Co particles observed on SiO₂-supported catalysts compared with Al₂O₃-supported catalysts. Khodakov et al. [48] have observed the same pore size effect for cobalt supported on mesoporous silicas. Recent TEM studies have shown that the Co particles exist as agglomerates of smaller particles [49,50]. Zhang et al. [51] found that Co supported on alumina with low acidity leads to higher activity and higher C₅₊ selectivity than Co supported on alumina with high acidity. Co supported on ammonium-treated and ammonium nitrate-treated alumina results in lower acidity and further higher activity and C₅₊ selectivity compared with the corresponding Co catalysts supported on untreated alumina [52]. The alumina used in the present work has low acidity.

The activity does not vary in the same way for all of the catalysts as the conversion is increased or water is added. For the Al₂O₃-supported catalysts the activity is slightly increased as the conversion is increased, but the catalysts deactivate rapidly as ~20% water or a larger amount of water is added. For the SiO₂-supported catalysts a large increase in activity is observed at increased conversion or when ~20% water is added, but again the catalysts deactivate rapidly at high partial pressures of water. The TiO₂-supported catalysts exhibit increased activity as the conversion is increased or ~20% water is added. Larger amounts of water reduce the activity, but a high concentration of water does not permanently deactivate this catalyst. The optimal partial pressure of water and the optimal inlet P_{H₂O}/P_{H₂} ratio for achieving the highest activity probably vary for the different supports. It is possible that water has a positive effect for all of the supported Co catalysts used in this study, but for some of the supports the deactivation is so rapid and large that it is not possible to observe the positive kinetic effect without examining the product gas continuously. The different behavior is probably due to different deactivation mechanisms for the various supports. For the Al₂O₃-supported catalysts, the deactivation is mainly due to surface oxidation or oxidation of highly dispersed phases interacting with the support [2]. Recently, Jacobs et al. [53] found that when 25% water or less is added, the negative effect for Co/Al₂O₃ was recovered when the water addition was terminated. XAS studies made of the samples after 25% water addition indicated that the structure of cobalt did not change. They proposed a kinetic effect below 25% water addition due to adsorption inhibition. At high pressures of water (above 28%), changes in cobalt structure were readily observed, and EXAFS confirmed that cobalt aluminate-like species were formed. Catalysts with smaller cluster sizes were found to be more sensitive to permanent deactivation from water [54]. The deactivation ob-

served for the SiO₂-supported catalysts has been proposed to be due to formation of cobalt silicates in the presence of water [10]. It has been found that with the addition of zirconia to the Co/SiO₂ catalyst, the cobalt-silica interactions decreased and were replaced by Co–Zr interactions that favor reduction of the catalyst at lower temperatures, thus increasing the activity [55]. For the TiO₂-supported catalyst no significant deactivation occurs. Another explanation for the impact of water may be differences in cobalt cluster size for the various supports. A decrease in the size of cobalt clusters results in a decrease in the extent of secondary reactions [56]. The activity and selectivity results imply that the nature of the supports is crucial when it comes to deactivation (because of interactions between Co and the support), but structural differences seem to be the prevailing consideration with respect to selectivities, and probably activities, for the various catalysts.

4. Conclusions

The effect of water on the selectivity and activity for 12% Co/Al₂O₃, 12% Co–0.5% Re/Al₂O₃, 12% Co/SiO₂, 12% Co–0.5% Re/SiO₂, 12% Co/TiO₂, and 12% Co–0.5% Re/TiO₂ has been studied in a fixed-bed reactor. The conversion was increased (producing more water) and varying amounts of external water were added to the feed during the Fischer–Tropsch synthesis. The water was found to have different effects, according to the type of support:

- For the Al₂O₃-supported catalysts the activity was almost unchanged as the conversion was increased, whereas the addition of external water deactivated the catalysts. The deactivation observed was greater at higher water partial pressures and only partly reversible after removal of the water. The addition of water resulted in greater deactivation for the Re-promoted catalyst.
- Increasing the conversion or adding ~20% water to the SiO₂-supported catalysts increased the activity, but also the rate of deactivation. Adding more water to the feed (~33%) increased the rate of deactivation even more. Only a relatively small part of the deactivation was recovered after water removal.
- For the TiO₂-supported catalysts an increase in conversion or the addition of ~20% water resulted in increased activity. Higher partial pressures of water resulted in decreased activity. No permanent deactivation was observed for the TiO₂-supported catalysts.
- Indigenous or added water led to a marked increase in C₅₊ selectivity and a decrease in CH₄ selectivity for all of the Co catalyst systems.
- Re increased the activity for all three supports and the C₅₊ selectivity for the SiO₂ and TiO₂ supports.

Acknowledgments

The Norwegian Research Council is acknowledged for financial support. The authors also thank E. Bjørgum and G. Carlsen for experimental assistance.

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