

Water as key to activity and selectivity in Co Fischer-Tropsch synthesis: γ -alumina based structure-performance relationships

Erling Rytter, ^{a,b} Øyvind Borg, ^{φ,a} Nikolaos E. Tsakoumis ^a and Anders Holmen^{*,a}

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

^b SINTEF Industry, N-7465 Trondheim, Norway

*Corresponding author. anders.holmen@ntnu.no

Abstract

Thirteen γ -alumina supports with different pore sizes and pore size distributions have been impregnated with cobalt and rhenium. The catalysts were tested for Fischer-Tropsch synthesis (FTS) under dry and enhanced water vapor pressure conditions. It is shown that there is a positive correlation between pore size and cobalt crystallite size of the reduced catalyst after incipient wetness impregnation as long as the pore size distribution is sufficiently narrow. There is a concurrent increase in C_{5+} with pore diameter due to higher chain propagation probabilities α_{3+} . Higher α values are ascribed to larger cobalt crystallites that promote CO activation resulting in higher surface coverage of CH_x monomers. Adding water vapor to the syngas feed has a strong positive effect on selectivity to higher hydrocarbons and activity. Water imposes a significant enhancement of α_1 that is attributed to higher relative cobalt surface coverage of $H_2O(OH^-)$ and CH_x relative to hydrogen. Small pores are susceptible to condensation of water during FTS.

^φ Present address: Statoil Research Center, Trondheim, Norway

Introduction

Supported cobalt catalysts are widely studied and applied for conversion of synthesis gas in low-temperature (< 250 °C) Fischer-Tropsch (FT) synthesis. These catalysts provide high activity, high selectivity to long chain paraffins and low water-gas-shift (WGS) activity. It is common practice to add a noble metal promoter, typically platinum or rhenium, to optimize the performance of the catalyst. Both cobalt and the promoter are rather expensive, and optimal usage in the reactor is of crucial importance.

Cobalt in reduced state is the active component in the CO hydrogenation reaction. The catalyst activity largely depends on the degree of reduction of the metal precursor and the size of the metal particles, which control the number of catalytically active sites that are available (dispersion). It has also been shown that the TOF (turnover frequency, *i.e.*, CO hydrogenations per active site and time) is reasonably constant for Co particles larger than 5-6 nm.[1,2] However, the TOF is sensitive to the support, *e.g.*, α -alumina shows higher activity than γ -alumina for catalysts that have the same Co crystallite size.[3] Some efforts have been done to describe the actual shape and distribution of the cobalt particles or their oxide precursors, but so far it is a challenge to correlate this information with catalytic properties.[4,5] It has also been claimed that cobalt being in the *hcp* or *fcc* phase is important, with *hcp* as the most active.[6]

The most frequently used activity promoters are rhenium, platinum and ruthenium, although numerous others have been investigated. Rhenium was first reported added to a Co/titania catalyst by Mauldin [7] and to Co/alumina by Eri *et al.* [8] Mauldin and Varnado concluded that for the former system rhenium functions to increase cobalt oxide dispersion during catalyst preparation and to promote reduction of cobalt oxide to the active metal phase.[9] A similar conclusion was reached for the alumina supported system by Hilmen *et al.*[10] Diehl and Khodakov have reviewed promotion of cobalt FT-catalysts with noble metals.[11]

The type and structure of the support (catalyst carrier) influence the dispersion and consequently the activity of the FT-catalyst system. The most frequently used supports described in the literature are alumina, silica and titania.[12] These materials behave differently when cobalt is deposited and, moreover, there are huge differences in properties within each class of support. These differences manifest itself in variations in activity, but to a larger extent in the polymerization probability, *e.g.*, as detected by the C₅₊ selectivity, as well as in the selectivity effect and stability toward re-oxidation by water.[13,14,15,16,17] For all catalyst systems and process conditions known to the present authors, water added to the feed and indigenous water produced during synthesis result in enhanced selectivity to higher hydrocarbons. The C₅₊ selectivity increases with conversion due to a positive effect of produced water. It follows that comparison of catalytic properties for different catalysts should be carried out at the same conversion level. However, above 80 % conversion the selectivity drops as the WGS reaction significantly increases the hydrogen concentration. Conversion increases linearly with space-time at standard testing conditions.

Apparently, there is moderate effect of *produced* water on the activity. Nevertheless, in a recent paper it was suggested that water plays a key role in activation of CO by providing hydrogen to the oxygen

atom.[18] Adsorbed water presumably interacts with CO and lowers the energy barrier for CO activation, thereby enhancing the surface coverage of polymerization intermediates. Added water to the syngas may increase or decrease the catalyst activity.[19] More inert supports and large pore size supports exhibit a positive response. Most notable exception is medium to narrow pore size γ -alumina and silica that have negative response to water.[20] Further, there is a limit to the positive effect of water on activity as too high amounts result in decreased activity. No published kinetic expressions for FTS has taken these combined responses into account.

Alumina is probably the most intensively investigated support for Co FT-catalysis. It is well established that interaction between the different phases containing cobalt and/or aluminum plays an important role in the FT-chemistry. For example, it is commonly assumed under normal activation conditions that a fraction of the cobalt forms an irreducible cobalt aluminate spinel covering most of the surface.[21] Intrusion of Co^{II} into the alumina lattice has been observed to occur during reduction.[22] It is challenging to describe the pore structure of the support and the distribution of cobalt in the pores. The average properties of alumina, on the other hand, like pore size distribution, surface area, average pore diameter and pore volume, can easily be measured. It is likely that the pore geometry influences the catalytic properties, in addition to factors like the purity of the support and the phase. [23,24] The pore geometry effects appear, however, to be partly indirect in that the pore size influences the cobalt particle size and the interaction with the support. Increase in cobalt crystallite size and degree of reduction with increasing pore diameter was found when using a silica support.[25]

Although $\gamma\text{-Al}_2\text{O}_3$ is the most common alumina-based catalyst carrier, a number of transition phases occur before the thermodynamically stable α -alumina phase is reached. It has been shown that high temperature calcination accompanied by changes in pore geometry and partial transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ gives a catalyst with significant increase in selectivity.[26,27] Such treatment drastically reduces the alumina surface area, from typically 150-200 m^2/g to 5-15 m^2/g , and the dispersion and distribution of cobalt thereby becomes restricted by the low available surface area. By comparing the performance of catalysts on the γ - and α -alumina phases with the transition phases $\delta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$, it was found that the delta phase exhibits an unexpectedly high C_{5+} selectivity even great care was taken to compare performance for approximately same particle size.[28]

It has been reported that for comparable γ -aluminas with surface areas in the range 170-200 m^2/g , the C_{5+} -selectivity increases with pore volume and pore diameter.[24,29] This effect has been verified for a larger selection of alumina supports, and it was reported that the main parameter defining the selectivity is the cobalt crystallite size. For incipient wetness impregnation, a correlation was found between pore diameter and crystallite size. There appears to be a limit to the size effect, and the selectivity levels out at ca. 10 nm [2] and even a decline is found for large crystals.[30] It is intriguing, however, that even when controlling the cobalt crystallite size, different alumina phases show varying selectivities. In addition, there is moderate improvement in C_{5+} for large pore materials independent of the alumina phase and cobalt crystal size, pointing to some effect of the pore diameter after all. We observe that the detailed surface chemistry of the support plays a major role for tuning the FT-kinetics, and that a further investigation is due.

The present work concentrates on γ -alumina supports with large variations in pore sizes and pore size distributions. Differences in pore characteristics result in large variations in measured cobalt particle sizes. Effect of water is studied by adding water vapor during the FT-reaction. An attempt is made to unravel the relationship between pore structure and cobalt size with water response and selectivity.

Experimental

Catalyst preparation. Laboratory catalysts were prepared as described previously. [24,25] The catalyst oxide precursor was prepared by one-step incipient wetness co-impregnation of γ - Al_2O_3 with an aqueous solution of cobalt nitrate hexahydrate and perrhenic acid. Great care was taken to use chemicals with high purity only. The support and metal solution were mixed under ambient temperature and pressure conditions. Before impregnation, the support (53-90 μm) was calcined under air at 500 $^\circ\text{C}$ for typically 10 h in a static furnace. This re-calcination procedure is included to equilibrate the surface hydroxyl concentration of different samples after storage. The catalysts contain a nominal amount of 20 wt% cobalt and 0.5 wt% Re, as calculated assuming reduced catalyst with complete reduction of cobalt. ICP analysis of calcined samples showed cobalt content in the 16.3-18.9 wt% range and rhenium between 0.36 and 0.42 wt%. After impregnation, the catalyst precursor was dried in a stationary oven at 110-120 $^\circ\text{C}$ for 3 h. To ensure homogeneity, the sample was stirred gently every 15 min the first hour and every 30 min the last two. After drying, calcination was performed at 300 $^\circ\text{C}$ for 16 h, with a heating rate of 2 $^\circ\text{C}$ to the holding temperature. Both ramp rate, holding temperature and time, gas composition (humidity) and gas flow rate influence particularly the cobalt crystallite size and thereby optimization and reproducibility of the Fischer-Tropsch performance.[32] A total of 13 catalysts were prepared and numbered C1 to C13.

Fixed-Bed Catalyst Testing. The Fischer-Tropsch reactions were conducted in a fixed-bed reactor (stainless steel, 10 mm inner diameter). The apparatus is fully automated with four reactors in parallel. The samples were sieved (53-90 μm) and 1-2 g were diluted with inert silicon carbide particles (20.0 g, 75-150 μm) in order to improve the temperature distribution along the catalytic zone. An aluminum jacket was placed outside the reactor to secure isothermal conditions. The catalyst was reduced *in situ* in hydrogen at ambient pressure while the temperature was increased at 1 $^\circ\text{C}/\text{min}$ to 350 $^\circ\text{C}$. After 16 h of reduction, the reactor was cooled to 170 $^\circ\text{C}$. The system was then pressurized to 20 bar, and synthesis gas of molar ratio $\text{H}_2/\text{CO} = 2.1$ with 3% N_2 as an internal standard was added. The temperature was then increased slowly to the reaction temperature of 210 $^\circ\text{C}$. Space velocity was adjusted according to a reactor model to give a predicted carbon monoxide conversion level between 45 and 50 percent after 26 h time on stream (TOS). Water was vaporized, heated to reaction temperature and added to the feed at intervals in two concentration levels, 4,25 bar and 7,06 bar; simulating 46 and 64% conversion at the inlet, respectively.

Liquid products were removed in a cold trap, while heavy hydrocarbons were collected in a heated trap. The effluent gaseous product was analyzed for hydrogen, nitrogen, carbon monoxide, carbon dioxide, water, and C_1 to C_9 hydrocarbons using an HP5890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The C_{5+} selectivity was calculated by subtracting the amount of C_1 - C_4 hydrocarbons and carbon dioxide in the product gas

mixture from the total mass balance. Activity is reported as the hydrocarbon formation rate ($q_{\text{hydrocarbon}}/(g_{\text{catalyst}}h)$). The precision of the activity is 3% (2σ). To check for particle external mass transfer limitations, experiments with different catalyst loading, but constant diluted bed heights, were performed. The catalyst space velocity was unaltered, thereby operating at varying linear velocities. Selectivities at constant conversion measured after 100 h TOS show minimal variations.

Catalyst Characterization. Nitrogen adsorption/desorption isotherms were measured after outgassing at 300 °C overnight. The surface area was calculated from the Brunauer-Emmett-Teller (BET) equation, and total pore volume and pore size distribution were found by applying the Barrett-Joyner-Halenda (BJH) method.[33] The nitrogen desorption branch was chosen for pore size analysis. Hydrogen adsorption isotherms were obtained after evacuation 40 °C for 1h followed by reduction in hydrogen for 6h at 350 °C. Chemisorbed hydrogen was found from the isotherm recorded in the pressure interval 20 to 510 mmHg and extrapolation to zero pressure. Cobalt crystallite size was calculated by assuming spherical particles and no contribution from the rhenium promoter. Oxygen titration of reduced samples was performed by adding a series of oxygen pulses at 400 °C. Degree of reduction (DOR) was calculated assuming that metallic cobalt oxidized to Co_3O_4 . Measuring DOR is not trivial, and it has been reported that the present oxygen pulsing technique may underestimate the degree of reduction due to incomplete oxidation.[34]

Details on applied catalyst characterization equipment and procedures can be found in a previous report. [24]

Results and discussion

Catalyst characterization

Characterization of the catalysts has been reported previously [24] and key data are summarized in Table 1. Surface areas (SA) of oxide catalysts vary from 86 to 192 m^2/g and pore diameter (PD) from 5.7 to 23.7 nm with corresponding variation in pore volume from 0.19 to 0.62 cm^3/g . The large distribution in average pore data indicates a similar distribution of γ -alumina crystallite sizes. Due to low contrast for the support, no attempt was made to quantify the γ -alumina crystallite shapes by transmission electron microscopy. Reasonably enough, the pore values for each individual catalyst are generally somewhat lower than for the neat γ -alumina support. However, no reduction in pore diameter is seen for C10 that exhibits a very broad bimodal pore size distribution. This is ascribed to compensating effects of general reduction in pore size, with a possible pore blocking of some narrow pores during impregnation.

Table 1. Characterization of Co/Re/ γ -alumina catalysts.*

Catalyst sample	Type of support	Surface area (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)	Pore size distribution	Co particle size (nm)**	Degree of reduction (%)***
C1	Süd-Chemie	168	5.7	0.28	Very narrow	8.4	55
C2	Alcoa HiQ 7219CC	175	6.1	0.31	Narrow	8.0	59
C3	Puralox SCCa 40/195	143	7.1	0.30	Narrow	8.3	56
C4	Akzo CPR 11.000	165	7.9	0.34	Very broad	8.6	59
C5	Alcoa HiQ 7S10CC	86	7.9	0.19	Very broad	9.7	57
C6	Alcoa HiQ 7213CC	112	8.1	0.24	Narrow	8.5	58
C7	Pural NG	136	8.2	0.30	Very broad	9.5	59
C8	Akzo CPR 11.002	169	10.2	0.47	Medium broad	8.6	59
C9	Harshaw A-4100P	192	10.4	0.61	Broad/bimodal	9.1	63
C10	Puralox SCCa 45/190	149	11.6	0.51	Very broad/bimodal	10.2	60
C11	Puralox SCCa 20/190	148	11.6	0.50	Medium broad (Slightly bimodal)	9.5	61
C12	Puralox TH 100-150	123	18.3	0.62	Medium broad	11.3	70
C13	Puralox 190 UHP	92	23.7	0.57	Broad	12.6	71

* Data extracted from reference [24].

** From hydrogen chemisorption and adjusted for DOR.

*** From oxygen titration.

In general, the pore size distribution (PSD) of a catalyst and its support have the same shape. It is challenging to give a quantitative description of the large variation in pore size distributions, but in the table, we have given a qualitative description in terms of broadness and modality. Lack of a more accurate mathematical model is unfortunate as we find the pore size distribution to influence the catalytic performance. Four selected pore size distributions are shown on Figure 1 illustrating the variations; even within one series of materials from one alumina supplier.

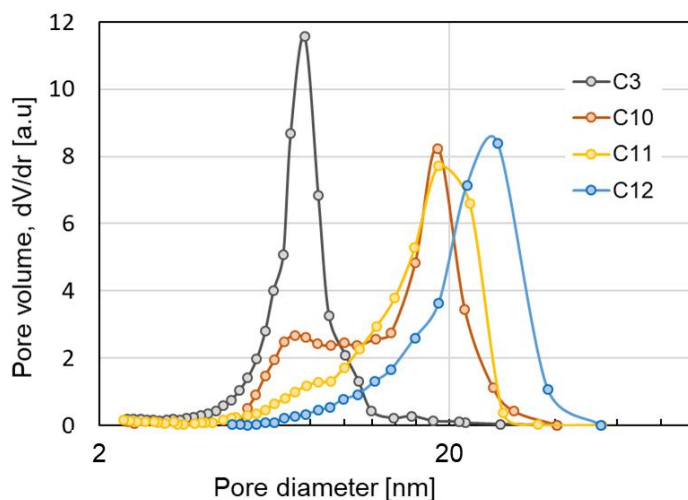


Figure 1. Pores size distribution for Puralox γ -alumina. Baselines have been adjusted.

Degree of reduction varies from 55 to 71%, increasing with pore size. Larger pores, *i.e.*, larger alumina crystallites, show less surface defects and give rise to a weaker metal-support interaction. Cobalt crystallite size varies between 8.0 and 12.6 nm. This range is at the peak of the volcano curve for selectivity [2,30] and only moderate effect of cobalt crystallite size on C_{5+} is expected. Previously, a positive correlation between cobalt crystallite size and average pore diameter has been indicated. [24] By correcting for degree of reduction, this correlation becomes rather significant, in particular when a few odd samples are omitted from the linear trendline; see Figure 2. It is concluded that wider pores give rise to larger cobalt crystallites. Although this might seem intuitive, the mechanism behind is beyond the scope of the present study. The four odd samples have very broad pore size distributions, confer C10 of Figure 1. Three of these have significantly higher cobalt sizes than expected. It appears that cobalt is preferentially deposited during drying and calcination in the larger pores of the distribution.

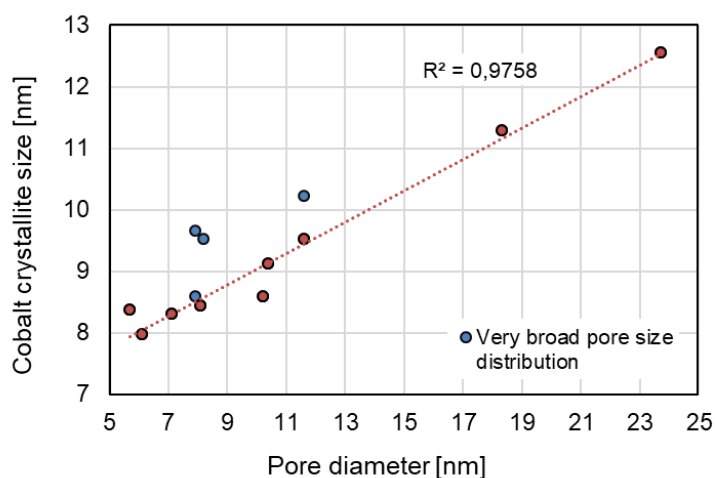


Figure 2. Cobalt crystallite size adjusted for degree of reduction as a function of average pore diameter of catalysts on γ -alumina. Trendline is without four data-points for catalysts with very broad pore size distributions.

The TEM image in Figure 3 illustrates both general features of Co-Al₂O₃ catalysts and characteristics of a wide pore alumina support; in this case Puralox TH 100-150 with average pore diameter 18.3 nm. Cobalt oxide crystallites are repeatedly found to be located in aggregates for catalysts on alumina and silica supports, and it has been found that the size of the aggregates correlates with porosity of the supports for catalysts prepared by incipient wetness impregnation. [35,36] It is, however, possible to influence the aggregate size through the impregnation method. [2] So far, there is little evidence for aggregate size playing an important role in FT synthesis. Perhaps more relevant is the comparably well-formed crystals of the alumina support. The γ -Al₂O₃ crystals are slightly needle formed with shortest dimensions in the 5-7 nm range and length extending 1-5x the needle diameter. This morphology is materially different from a similar micrograph of catalyst C11 where the alumina phase is composed of longer, thinner and less well-defined needles. [36]

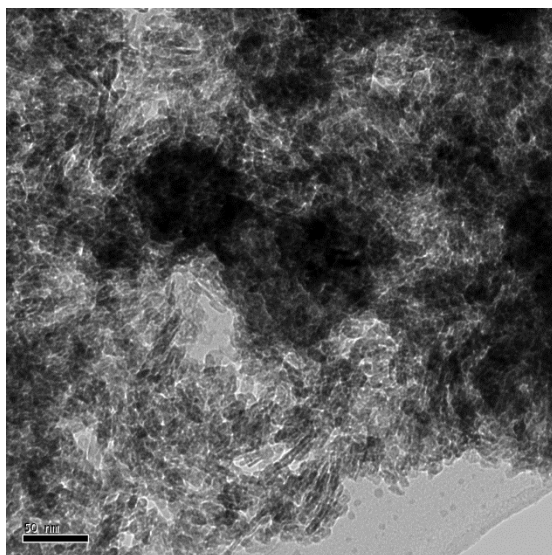


Figure 3. Bright-field TEM micrograph of catalyst C12 before reduction. Dark spots are cobalt; bar = 50 nm.

Fischer-Tropsch activity

The catalyst performance has been reported at integral reactor conditions therefore the term site-time yield is used. It has previously been found that the site-time yield of the Fischer-Tropsch synthesis for catalysts C1 to C13, at the given process conditions after 8h on stream, vary within a fairly narrow range from 0.045 to 0.073 s⁻¹ [1,24] A major parameter influencing the site-time yield is the residual content of sodium in the support from 20 to 113 ppm. Taking the effect of sodium into account, the spread is only ± 0.005 s⁻¹.

The present study focuses on the influence of water on FT performance by adding water during the run. The procedure and effect for the C11 catalyst is shown in Figure 4. The run is divided into five periods A-E:

- A. Synthesis gas with flow rate 250 ml/min.

- B. Synthesis gas with reduced space velocity to give an initial CO conversion of ca. 50% at 30 h time-on-stream (TOS).
- C. Keeping the synthesis gas flow-rate from period B and adding water vapor to give 21% water vapor pressure at the reactor inlet.
- D. Increasing the water vapor pressure to 35%.
- E. Returning to the conditions of period B.

This procedure is compatible with previous reports on the effect of water for γ -alumina, silica, titania and carbon nanofiber. [13,20,37,38] The response to water for catalyst C11 is typical for a medium to wide pore γ -alumina. The CO conversion in period C increases initially just after water addition before it levels out at close to the expected level between periods B and E due to deactivation. Increased activity follows from the consorted vinylene mechanism encompassing water assisted activation of CO. [18] On the other hand, adding more water suppresses the conversion; presumably due to oversaturation of the cobalt surface giving reduction in the concentration of polymerization monomers.

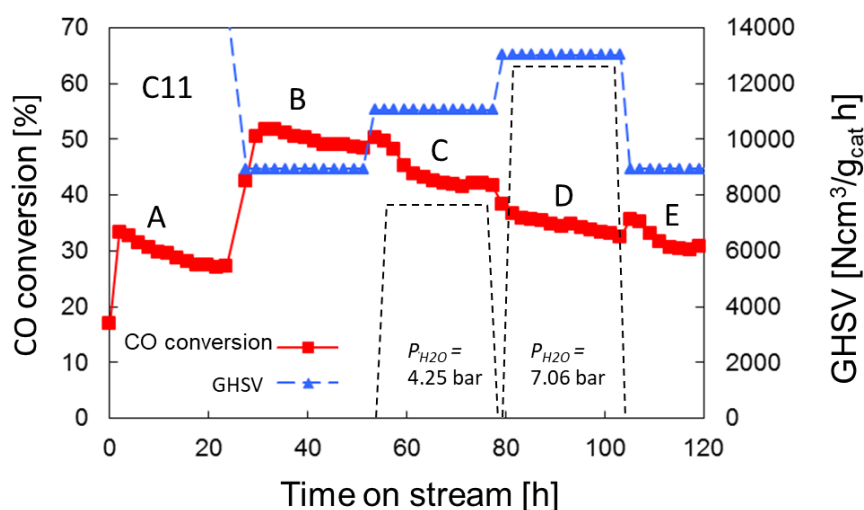


Figure 4. Effect of water addition on CO conversion during FT-synthesis for Co/ γ -alumina catalyst C11.

Parallel to the responses to water on activity, there is evidently a significant catalyst deactivation. The conversion is reduced from 49% at the end of reference period B to 35% at the beginning of period E; during just 55 h TOS. The CO conversion in the beginning of period C is 50%, and taking added water into account, the water vapor pressure corresponds to a conversion of 73% for a dry run; or $P_{H_2O}/P_{H_2}=1.3$. Similarly, 40 % CO conversion in the start of period D corresponds to 78% conversion for a dry run; $P_{H_2O}/P_{H_2}=1.7$. (Please note that the actual CO conversions are as shown in the figure, and the simulated higher conversions are only given to illustrate the corresponding level of the water vapor pressure in a dry run). These water levels are far higher than normally experienced for fixed-bed FT-synthesis, but the P_{H_2O}/P_{H_2} ratio still is within the operating range for microchannel and slurry bubble column reactors. [19] Therefore, the strongly enhanced deactivation is somewhat surprising.

Oxidation of the smallest and most reactive cobalt crystallites is the likely cause, consistent with previous TEM studies under similar conditions. [15,39] Further, it is known that sintering is a major deactivation mechanism during the initial phase of FT-synthesis, [40,41,42] and sintering most likely is enhanced by water. Formation of aluminates between cobalt and the support is probably also enhanced by water vapor. [43] Comparison with a dry run in Figure 5 puts the enhanced deactivation into perspective.

Effect of pore size and pore size distribution on activity

Performance of two catalysts with different pore size distributions are compared in Figure 5, *cf.*, the distributions in Figure 1. Both have the same average PD, but C10 shows a distinct and well separated bimodal distribution compared to C11. The average crystallite sizes are about the same; 10.2 and 9.5 nm, respectively. Evidently, the catalyst that contains a significant contribution of narrow pores has a more negative response to water added in periods C and D. This is in line with the previous suggestion of condensation of water in narrow pores during FT-synthesis. [19] Note that the bimodal catalyst shows less deactivation after water has been removed from the feed. We speculate that cobalt particles in pores filled with water actually are less prone to deactivation as they are partly exempt from the Fischer-Tropsch reaction and less exposed to local heating.

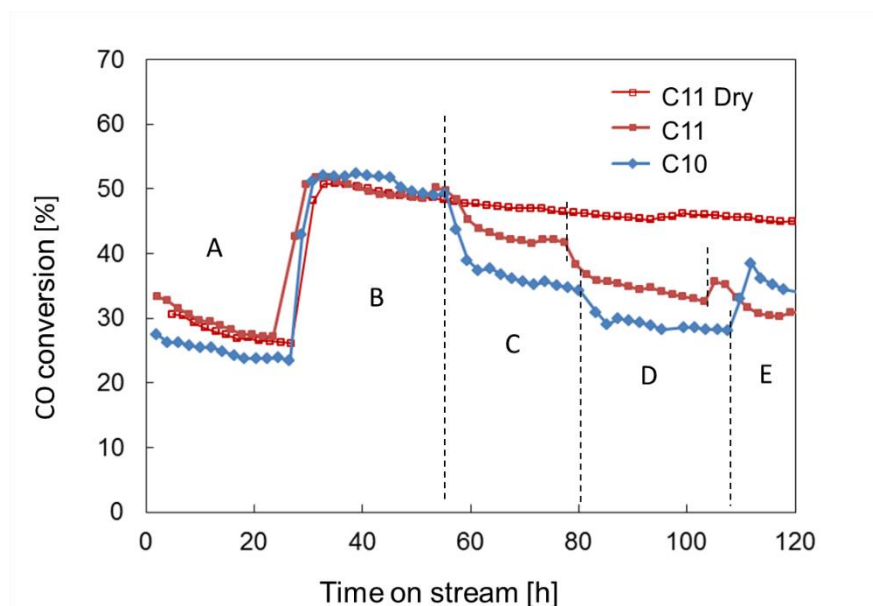


Figure 5. Comparison of two Co/ γ -alumina catalysts with different pore size distributions.

Further evidence for the effect of pore size and pore size distribution is found in Figure 6 where six catalysts are compared, all having nearly the same Co crystallite sizes; 8.3-9.1 nm. Catalysts C8 and C9 also have the same average PD; 10.2 and 10.4 nm, respectively. It is as expected that C9 with a broad bimodal pore size distribution is most affected by water compared to the medium broad distribution of C8. Catalyst C3, with a narrow distribution of pores, has practically no reduction in activity for the lowest level of water vapor addition. There is apparently an exempt for catalyst C1 that has medium water vapor response but has very narrow pore distribution. However, C1 has the lowest

average PD of all catalyst; 5.7 nm compared to 7.1 nm for C3 and 10.2 for C8. Again, pore condensation in narrow pores accounts for the relative position of catalyst C1 as it is more responsive than expected merely from the well-defined pores. Catalyst C4 evidently is most responsive to water. This catalyst is characterized by the clearly broadest distribution of pores of the six catalysts, in particular when the moderate PD is taken into account. We conclude that smaller pores as part of a broad pore size distribution is the dominating cause of negative impact of adding water to the feed during FT-synthesis. It follows that catalysts with low average PD also are susceptible to this negative effect.

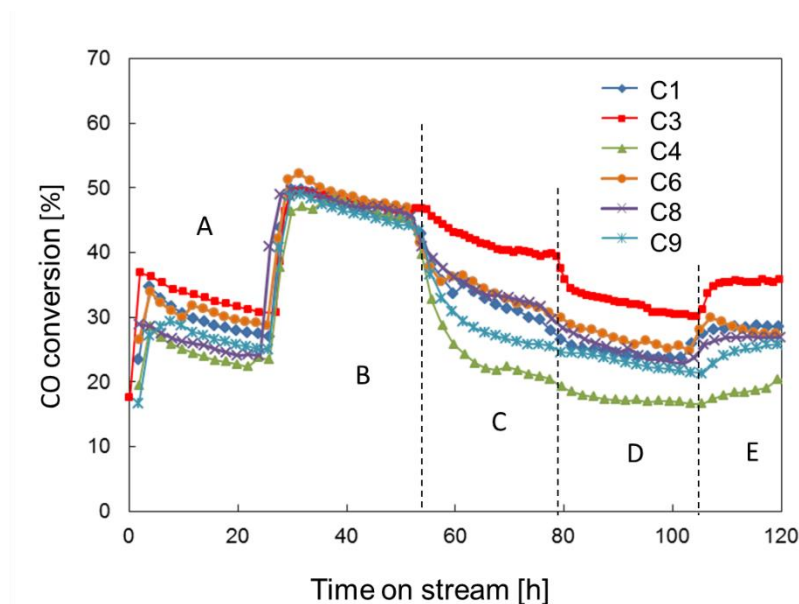


Figure 6. Comparison of six Co/ γ -alumina catalysts with different pore sizes and pore size distributions.

From the above examples it seems that we are left with essentially neutral or negative response to water vapor addition on catalyst activity for γ -alumina supports; in contrast to the positive response found for titania and some silica supports. [13] This is, however, not the case. Figure 7 summarizes conversion diagrams for catalysts exhibiting neutral or positive activity responses. Catalysts C11, C12 and C13 are characterized by, in that order, increasing PD from medium wide to very wide, and increasing cobalt crystallite size from 9.5 nm to 12.6 nm. The PSD is medium broad, somewhat broader for C13, but in a range that does not include any significant narrow pores. Adding 4 bar water vapor to the feed gives corresponding changes in the CO conversion, *i.e.* favoring wide pores with large cobalt crystallites. The PSD is less important as long as the fraction of small pores, say below 8 nm, are minimized. The positive response of C7 does not follow the main trend in pore properties and remains unexplained. A clue might be found in this aluminas origin, being based on calcination of boehmite, $\text{AlO}(\text{OH})$, with particularly regular crystal shapes.[44] Oversaturation of water is clearly seen for all catalysts when 7 bar water is added. It seems like some catalysts have a particularly steep decline in activity at these conditions although there is no obvious correlation with pore size or pore size distribution.

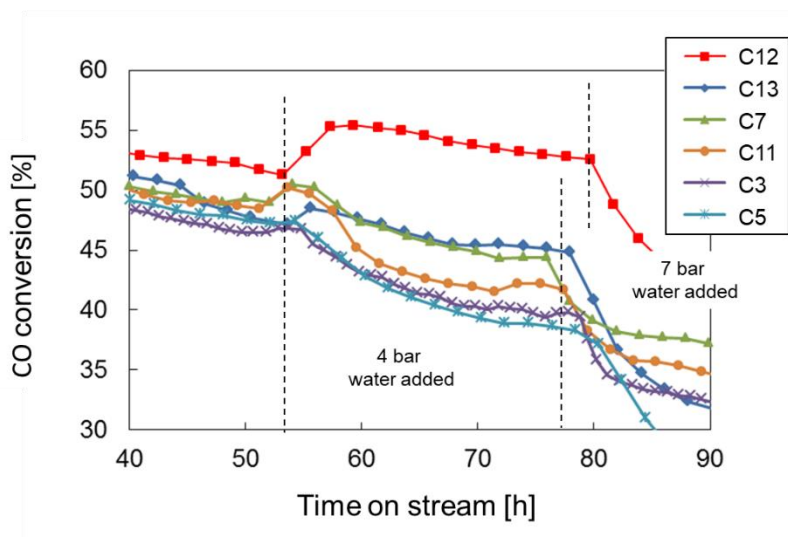


Figure 7. Co/ γ -alumina catalysts with neutral or positive activity response to added water.

Effect of cobalt crystallite size on activity

In the introduction, references are given to the well-known cobalt structure-sensitivity in FT-synthesis for a given support. Specifically, increase in site-time yield is found from 4 and to approximately 8 nm in crystallite size. [1] From the present data it is challenging to elucidate with confidence the effect of cobalt crystallite size on catalyst activity during FT synthesis with different levels of water vapor pressure. Nevertheless, some indications are identified. It was noted above that positive water vapor effects are found for cobalt catalysts with crystallite size on the high end in the present investigation, albeit this follows from high PD and incipient wetness impregnation.

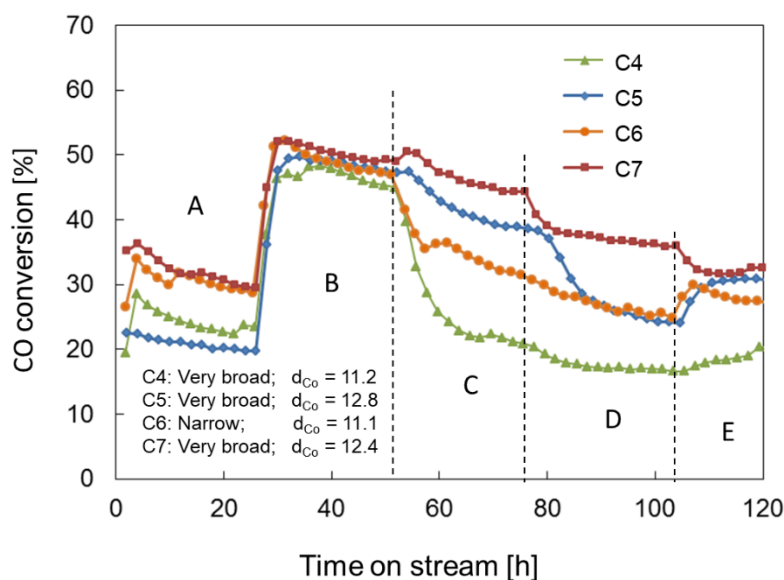


Figure 8. Effect of water vapor addition on CO conversion for catalysts that coincide in pore diameter. Specified cobalt particle sizes are uncorrected for DOR.

An attempt to compare catalysts that coincide in pore diameter is shown in Figure 8; PD = 7.9-8.2 nm. Period B shows that the catalysts have the same activity, *i.e.*, corresponding to the experimental uncertainty. There are two classes of cobalt crystallite diameters, 11.1 and 11.2 nm vs. 12.4 and 12.8 nm; not very far apart, but still a difference of 1.2 to 1.7 nm. Although the variation in crystallite sizes is moderate, the data indicates that the larger crystals respond more positively to water vapor. Variations in PSD does not alter this observation. In fact, from pore size distribution catalyst C6 is expected to be most favorably affected by water, but this appears to be outweighed by the difference in Co size.

C₅₊ selectivity

Unlike activity, the selectivity to higher hydrocarbons increases with partial pressure of water irrespectively of water being added or as a consequence of conversion. [19] This improved selectivity has been attributed to higher concentration of propagating CH_x monomers compared to the number of growing chains as water activates CO. [18] However, it takes a few hours for the system to equilibrate and reach the full effect of added water. [32] Therefore, comparison of C₅₊ values are performed at the end of each of the periods A-D. The measured values are listed in Table 2. Without exception, C₅₊ increases as conversion is adjusted upward to 50% between periods A and B and further to periods C and D when water vapor is added in successively larger amounts. The values are compared with a Co/Re catalyst on α -alumina in Figure 9.

Table 2 Fischer-Tropsch selectivities to C₅₊ of Co/Re/ γ -alumina catalysts at the end of each test period.

Catalyst sample	Type of support	C ₅₊ selectivity [C%]			
		Period A	Period B	Period C	Period D
C1	Süd-Chemie	77.0	78.5	81.2	82.2
C2	Alcoa HiQ 7212CC	77.4	79.2	81.8	83.1
C3	Puralox SCCa 40/195	78.8	79.7	83.2	83.9
C4	Akzo CPR 11.000	77.2	79.5	79.7	81.1
C5	Alcoa HiQ 7S10CC	77.4	80.9	84.6	85.3
C6	Alcoa HiQ 7213CC	78.5	80.6	83.2	84.4
C7	Pural NG	78.7	80.9	85.5	86.9
C8	Akzo CPR 11.002	78.4	80.3	82.9	84.1
C9	Harshaw A4100P	78.8	80.7	82.8	84.1
C10	Puralox SCCa 20/190	79.6	82.6	84.9	85.8
C11	Puralox SCCa 45/190	79.3	81.7	86.0	87.3
C12	Puralox TH 100-150	81.3	84.3	89.0	89.9
C13	Puralox 190 UHP	78.7	80.9	85.4	86.5

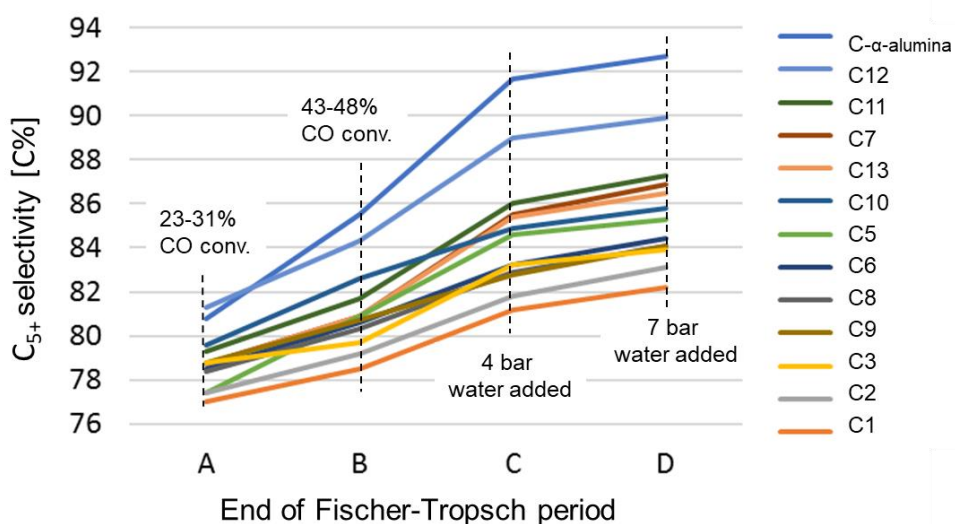


Figure 9. Fischer-Tropsch selectivities to C₅₊ of Co/Re/alumina catalysts at the end of each test period.

As expected from previous reports on α -Al₂O₃, [28] this more inert support gives high selectivities to long hydrocarbon chains; approaching values for titania. The performance of α -alumina in FT-

synthesis will be addressed in a separate paper. CO conversion ranges in the dry periods A and B are indicated on the figure. There are two exceptions; α -Al₂O₃ in period A is at 10% conversion, explaining the low selectivity compared to catalyst C12 at this point. The latter catalyst in period B is at 52% conversion, lifting the line for C12 somewhat through periods B-D. We have previously reported that C₅₊ selectivity response to water vapor increases with pore width by comparing catalysts C3, C11 and C12 and labeled them narrow, medium and wide pore catalysts.[19] This is compatible with the even larger response of α -alumina. The full γ -alumina dataset of increase in C₅₊ with moderate addition of water vapor is plotted in Figure 10 against pore diameter. Although there certainly is a trend, the correlation is not that great anymore. It is misleading that the three previously studied γ -alumina supports (red markers) make a steep line with α -alumina.

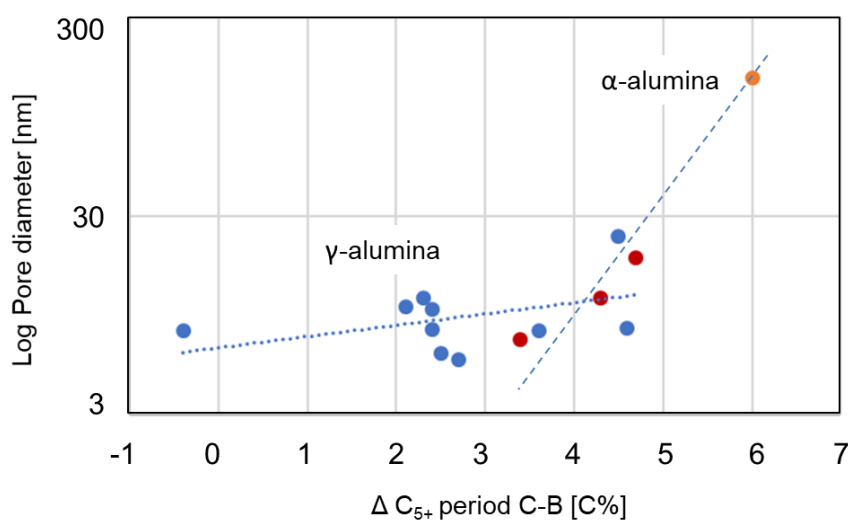


Figure 10. Response to C₅₊ selectivity by adding water vapor in period C as a function of pore size.

Nevertheless, it is still likely that pore size and surface acidity play important roles in determining selectivity in FT-catalysis. Indeed, plotting the C₅₊ values in the dry period B gives a better fit to pore size; see Figure 11. An outlier with low selectivity for the sample with very large pore diameter is not compatible with the present comprehension of pore size influence. No obvious trend is found based on pore size distributions.

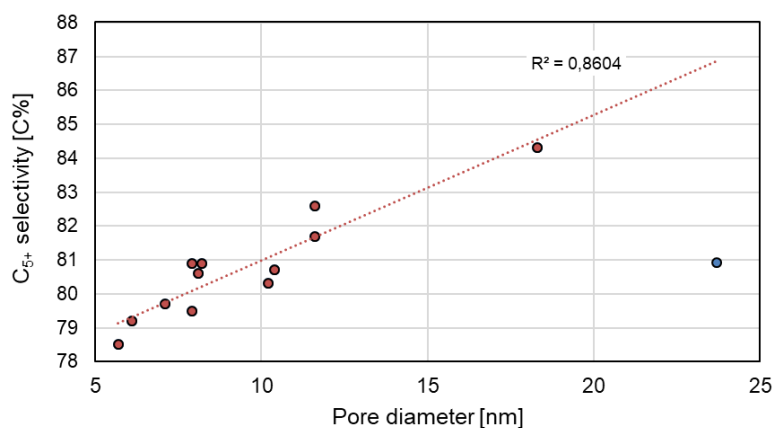


Figure 11. C₅₊ response to pore diameter in dry period B

An attempt was made to correlate the water vapor responses to other catalytic properties. As shown in Figure 12, a surprisingly good fit was found between the effect of added water on C₅₊ selectivity and conversion. That the conversion is reduced for most catalysts when water is added to the syngas feed is somewhat misleading as no correction is made for deactivation during period C and a lower total pressure of syngas. It is reasonable to believe that selectivity and activity enhancements have the same mechanistic origin. This fits with our model of water activation of CO and the impact CH_x monomer concentration has on FT-synthesis.[18,45] An increase in monomer concentration favors both chain growth and chain propagation rate. The crucial question then becomes: Why does some catalysts, essentially with wide pores, respond more favorably to water molecules with subsequent CO activation?

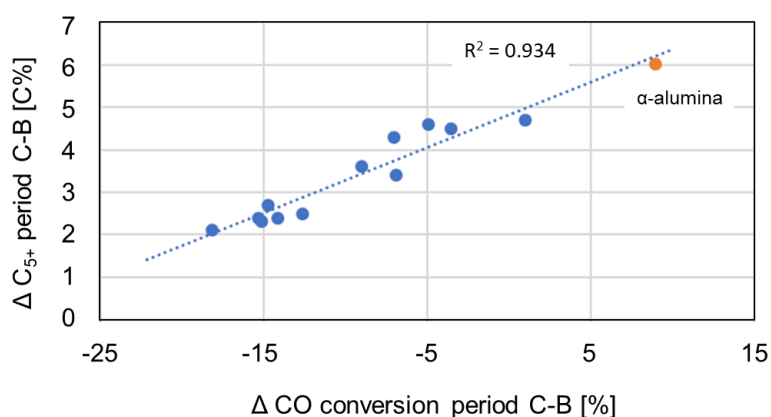


Figure 12. C₅₊ selectivity vs. CO conversion response to water added to syngas (Catalyst C4 has been omitted).

Chain propagation probabilities

In the section above, it was found that there is a positive correlation between pore size and C₅₊ selectivity. At least in part, this is ascribed to an increase in cobalt crystallite size, but also to more well-ordered crystallites with less defects. Previously, this was tentatively explained using a strain model whereby interaction with the support becomes more relaxed as the pore size, *i.e.*, crystallites of the support, becomes larger. [46] Addition of water mainly enhances CO activation with accompanying higher total reaction rate and improved C₅₊ selectivity. There are notable exceptions for small pores and large pore size distributions ascribed to condensation of water. Larger cobalt crystallites appear to respond more favorably to addition of water.

In order to comprehend the selectivity variations in more depth, chain propagation probabilities have been calculated; specifically, α_1 , α_2 , α_3 and α_4 . The procedure has been described previously. [45] These probabilities describe different steps of chain initiation and propagation:

α_1 : Fraction of CH_x monomers that combine with another CH_x monomer to give C₂H_y relative to being hydrogenated to CH₄. Another way of expressing this alpha is the relative propensity for monomers to

initiate a growing chain relative to being fully hydrogenated. A critical factor for α_1 is hydrogen coverage on the cobalt surface, while the concentration of monomers (high activity) is of lesser importance. The last interpretation is not obvious. [45]

α_2 : Fraction of C_2H_y that picks up a new monomer to give C_3H_z relative to being terminated. C_2H_y is different in chemical nature than subsequent longer chains and behaves very differently. Only a very low portion of the C_2H_y entities terminate, and then to ethane.

α_3 and α_4 : Probabilities of the first steps of chain propagation relative to termination.

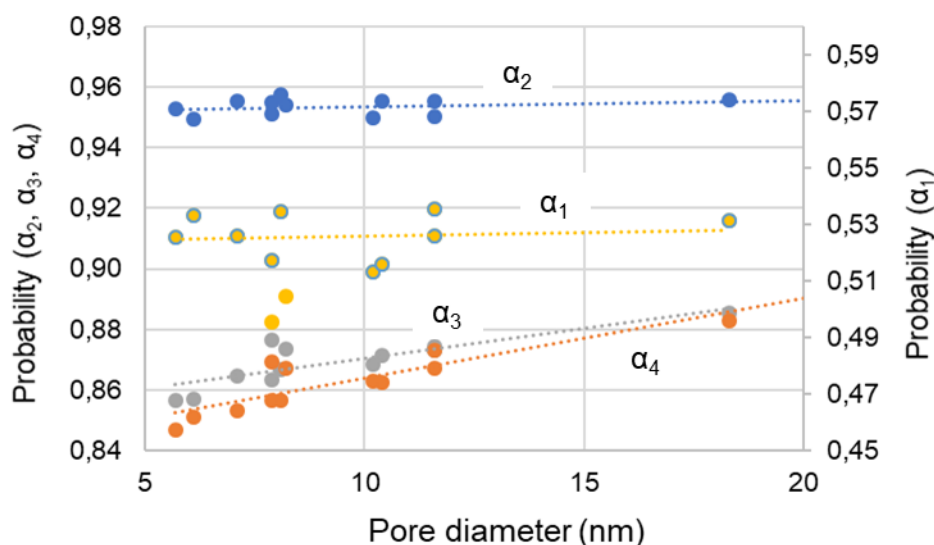


Figure 13. Effect of pore diameter on chain growth probabilities during dry period B. (Two low point for α_1 are exempt from trendline. They correspond to very broad pores size distributions).

The effect of pore size on the alpha values in test period B is shown on Figure 13. The trends parallel what was obtained for a large series of catalysts when the alphas were plotted as a function of C_{5+} . [45] There are clear correlations between higher alphas and long chain selectivity; as well as pore size. As the catalyst activity increases, more monomers are formed giving higher concentration of the CH_x pool. [47] These monomers are then more easily incorporated into the growing chain. [48,49]

In both the previous work of Lögdberg *et al.*, [45] and in the present work there is a slight increase in α_1 with higher C_{5+} . This increase was interpreted in terms of separate methanation sites. An alternative explanation is that the relative surface coverage of hydrogen decreases. This is in accordance with observed olefin/paraffin ratios that decrease with higher methane make. [2] α_2 is almost invariant to catalyst morphology. It appears that as long as an unsaturated C_2 specie, e.g. vinyl [18] is formed, further reaction toward propagation or termination is structure insensitive. This complies with a recently proposed mechanism where a C_2 intermediate can be hydrogenated to ethylidene or ethene depending on whether the α or β carbon atom of a vinyl fragment is hydrogenated. [18]

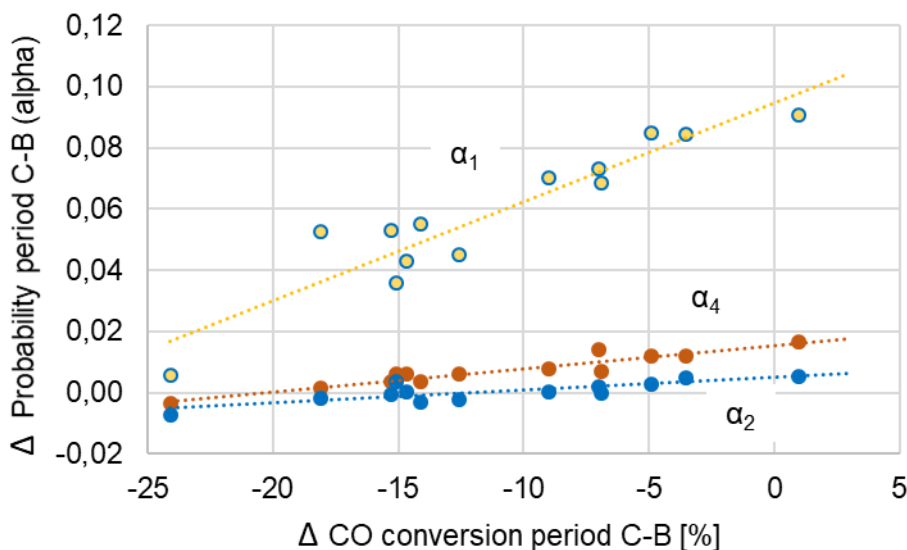


Figure 14. Chain growth probability responses vs. CO conversion response to water added to syngas.

Deconvolution into separate alpha values of the selectivity effect of water between period C with added water and dry period B, see Figure 12, is shown in Figure 14. The partial pressure of water added is the same for all experiments, but the response to activity is widely different for the different catalysts. The linear trends in Figure 14 show that all catalysts respond coherently to water with regard to selectivity and activity increase, again confirming previous results. According to the CH_x pool model, high CO activation rate impacts chain growth positively. It follows that water enhances CO activation, [48,50,51] see also the developed “consorted vinylene mechanism for cobalt Fischer-Tropsch synthesis encompassing water assisted CO-activation”. [18] However, the individual chain growth steps respond differently.

From the observed insensitivity of α_2 to pore size changes, it is reasonable that this propagation step shows moderate response to water. That there is a positive effect might stem from higher monomer concentration. Nevertheless, an effect of hydrogen coverage cannot be ruled out as C_2 terminates primarily to ethane, *i.e.*, a saturated product. This is contrary to C_3 and C_4 that terminate dominantly to α -olefins. The increase in α_4 is consequently ascribed solely to monomer surface coverage. The water response is clearly most significant for the initiation step. Less methane is formed as water is added and more chains are initiated. We suggest that this is a synergistic effect. As more water, and/or hydroxyl, groups and CH_x monomers cover the surface, the hydrogen coverage is suppressed. Simultaneously, higher monomer concentration favors C_1 - C_1 coupling.

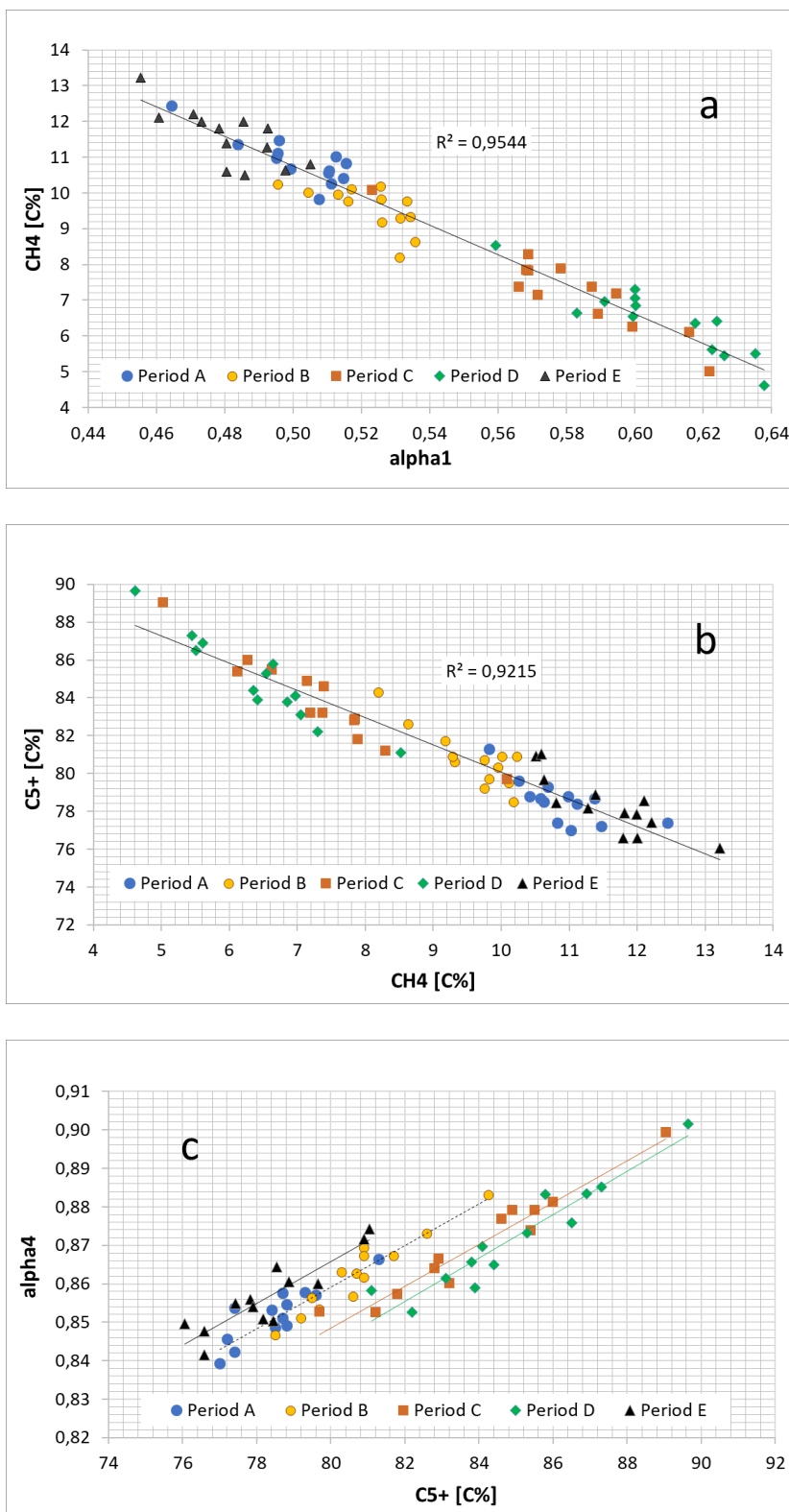


Figure 15. a) Methane selectivity as a function of chain growth probability α_1 ; b) C₅₊ selectivity as a function of CH₄ selectivity; c) Chain growth probability α_4 as a function of C₅₊ selectivity.

Looking at the entire dataset of 260 entries, *i.e.*, alpha values for all catalysts in five test periods, gives credit to the analysis above. Figure 15a shows that there is a close to linear correlation between CH₄ selectivity and α_1 , irrespective of the nature of the catalyst support, conversion level and water partial

pressure. In other words, α_1 is mainly dictated by hydrogenation of CH_x species, and any consequence of C_1 - C_1 coupling is less obvious. It is as expected that water addition enhances α_1 and suppresses methane formation. A closer look at the experimental periods shows a gradual increase in α_1 in the sequence $\text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{D}$ as the water partial pressure increases; first due to higher conversion and thereafter water vapor addition. Period E, returning to the period B gas feed conditions, but with CO conversion similar to period A due to deactivation, is apparently an exception. It seems as if deactivation, possibly caused by oxidation of fine cobalt crystallites, for unknown reasons promotes methane formation.

A linear response between CH_4 and C_{5+} , as in Figure 15b, was previously taken as a verification of the CH_x pool model. Methane and higher hydrocarbons are interlinked and do not proceed through entirely independent reactions. The sequence of the test periods is the reciprocal of Figure 15a; it is α_1 that is most sensitive to water.

A well-defined linear correlation was previously found between the C_{5+} selectivity and α_4 . [45,47] Figure 15c indicates that this statement should be modified. Four distinct trendlines are found to describe the data. The stippled line represents the periods A and B that has not been exposed to enhanced water partial pressure. With added water there is a successive increase in C_{5+} for periods $\text{B} \rightarrow \text{C} \rightarrow \text{D}$ for a given α_4 . Therefore, the response to water for the selectivity to higher hydrocarbons is not solely dictated by the chain growth probabilities α_{3+} , but to a large extent by the initiation reaction described by α_1 ; cf. Figure 15a. Deactivation by water preserves the bulk chain growth probabilities; it is higher hydrogen coverage and methane production that shift the distribution toward lighter products.

Conclusions

The conclusions have been derived specifically for Fischer-Tropsch synthesis of Co/Re/ γ -alumina catalysts. They are consistent with published data for unpromoted catalysts and catalyst on other supports, and therefore of universal value.

- Cobalt particle size increases with pore size of the support material, specifically γ -alumina, when deposited through incipient wetness impregnation, drying and calcination.
- For broad or bimodal pore size distributions, cobalt preferably is deposited in the larger pores by the incipient wetness impregnation method.
- Site-time yield is essentially constant for cobalt crystallites in the range 8-13 nm for supports with large variations in pore size and pore size distribution.
- Broad pore size distribution in the catalyst causes a strong negative impact on catalyst activity when water vapor is added to the syngas feed.
- Narrow pores are most likely susceptible to condensation of water although direct experimental evidence is lacking.
- A negative impact of water vapor on activity is found for catalysts with narrow average pore size.
- Well adapted pores size distribution, wide pores and sufficiently large cobalt crystallites causes a positive response on activity during addition of water vapor in moderate concentrations.
- Water vapor pressure increases the selectivity to higher hydrocarbons with no apparent limit for the partial pressure.
- C_{5+} selectivity increases with pore diameter of the catalyst.
- There is a positive, but moderate, correlation between C_{5+} selectivity response to added water and pore diameter.
- A concurrent response for C_{5+} selectivity and activity on added water implies a common mechanistic origin suggested to be water activation of CO which impacts the concentration of polymerization monomers.
- The chain growth probabilities α_{3+} increase significantly as the pore diameter becomes wider. It follows that larger cobalt crystallites are more effective in CO activation.
- Water increases the α_1 value significantly. This is attributed to suppressed hydrogen coverage on cobalt.
- Increase in C_{5+} with water partial pressure is mainly due to higher α_1 and only to a minor extent to α_{3+} .
- Deactivation by water reduces C_{5+} and decreases α_1 indicating higher hydrogen coverage.

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