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Review

## Design, synthesis, and use of cobalt-based Fischer–Tropsch synthesis catalysts

### Enrique Iglesia\*

Department of Chemical Engineering, University of California, Berkeley, CA 94720, USA

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#### Abstract

Catalyst productivity and selectivity to  $C_{5+}$  hydrocarbons are critical design criteria in the choice of Fischer–Tropsch synthesis (FTS) catalysts and reactors. Cobalt-based catalysts appear to provide the best compromise between performance and cost for the synthesis of hydrocarbons from CO/H<sub>2</sub> mixtures. Optimum catalysts with high cobalt concentration and site density can be prepared by controlled reduction of nitrate precursors introduced via melt or aqueous impregnation methods. FTS turnover rates are independent of Co dispersion and support identity over the accessible dispersion range (0.01–0.12) at typical FTS conditions. At low reactant pressures or conversions, water increases FTS reaction rates and the selectivity to olefins and to  $C_{5+}$  hydrocarbons. These water effects depend on the identity of the support and lead to support effects on turnover rates at low CO conversions. Turnover rates increase when small amounts of Ru (Ru/Co < 0.008 at.) are added to Co catalysts.  $C_{5+}$  selectivity increases with increasing Co site density because diffusion-enhanced readsorption of  $\alpha$ -olefins reverses,  $\beta$ -hydrogen abstraction steps and inhibits chain termination. Severe diffusional restrictions, however, can also deplete CO within catalyst pellets and decrease chain growth probabilities. Therefore, optimum  $C_{5+}$  selectivities are obtained on catalysts with moderate diffusional restrictions. Diffusional constraints depend on pellet size and porosity and on the density and radial location of Co sites within catalyst pellets. Slurry bubble column reactors and the use of eggshell catalyst pellets in packed-bed reactors introduce design flexibility by decoupling the characteristic diffusion distance in catalyst pellets from pressure drop and other reactor constraints. © 1997 Elsevier Science B.V.

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#### 1. Introduction

The Fischer–Tropsch synthesis (FTS) is a surfacecatalyzed polymerization process that uses  $CH_x$  monomers, formed by hydrogenation of adsorbed CO, in order to produce hydrocarbons with a broad range of chain length and functionality. Chain growth occurs by addition of surface methylene species to adsorbed alkyl groups; these alkyl groups can undergo  $\beta$ -hydrogen abstraction to form linear  $\alpha$ -olefins or hydrogen addition to form *n*-paraffins on Co catalysts [1,2].  $\beta$ hydrogen abstraction is a reversible chain termination step at typical Fischer–Tropsch synthesis conditions and the readsorption of  $\alpha$ -olefins leads to the reinitiation of alkyl surface chains and to the formation

<sup>\*</sup>Corresponding author. Fax: (+1-510) 6424778; E-mail: iglesia@cchem.berkeley.edu

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Scheme 1. Chain growth pathways and possible secondary reactions of olefins in the Fischer-Tropsch synthesis.

of larger hydrocarbons [3-8]. The proposed mechanism for chain growth in FTS and some potential secondary reactions (olefin hydrogenation, hydrogenolysis, and hydroformylation) are shown in Scheme 1. These reaction pathways are well established for Co and Ru FTS catalysts. On these catalysts, light hydrocarbons consist mostly of linear  $\alpha$ -olefins and heavier products are predominantly paraffinic, unless hydrogenation or isomerization sites are present. Fe-based catalysts, which are usually operated at higher temperatures, show higher selectivity to oxygenates and branched hydrocarbons, suggesting more complex termination pathways and secondary reactions, but chain growth pathways remain similar to those described in Scheme 1[5]. In particular, CO insertion termination pathways that form alcohols and  $\gamma$ -hydrogen abstraction steps leading to internal olefins become much more prevalent on Fe catalysts because of the higher reaction temperature and multicomponent surfaces typical of Fe-based Fischer-Tropsch synthesis. FTS products follow Flory-type carbon number distributions when chain growth and termination rates are independent of chain size. In such cases,

the logarithm of the molar hydrocarbon size distribution is proportional to chain size. Reported chain growth kinetics, however, often depend on chain size and lead to non-Flory carbon number distribution on Co, Ru, and Fe catalysts [3–6,9–11].

In this review, we describe the effects of the size of metal crystallites, the support identity, and the presence of an alloying element on the turnover rate and selectivity on supported Co catalysts. These effects arise at the level of a catalytic site and reflect the influence of site structure, composition, and electronic properties on the rate of the primary chain growth catalytic steps. In addition, we explore the subtle effects of secondary reactions, such as  $\alpha$ -olefin readsorption and hydrogenation, and of diffusional restrictions on chain growth pathways; these processes influence FTS selectivity and introduce catalyst design parameters unavailable in kinetic-limited catalysts. These effects occur at the level of a catalyst pellet and our research attempts to exploit intrapellet concentration gradients and radially non-uniform catalyst pellets in order to control the selectivity of chain growth reactions. Water, a reaction product in FTS,

influences chain growth selectivity and on some catalysts, also the rate of the primary CO hydrogenation reaction.

In the characteristic length scale of a catalytic reactor, we discuss the use of slurry bubble column reactors in order to decouple the chemical design of catalyst pellets for optimum selectivity from the pellet size restrictions imposed by pressure drop considerations within packed-bed reactors. Recent advances in the design of slurry reactors [12–14] have increased the economic incentives for their application in industrial FTS practice. These reactors have also restored the pre-eminent importance of surface reactions in FTS by lessening the significant heat and mass transfer disguises common in packed-bed reactors.

The details of the experimental and simulation methods used in the results reported in this review have been reported in detail elsewhere [3–8,15,16]. Results mentioned without references were obtained in our laboratory.

## 2. Design of supported cobalt catalysts for the Fischer–Tropsch synthesis

Fischer–Tropsch synthesis catalysts with high volumetric productivity decrease reactor volume requirements and improve significantly process economics. In general, volumetric productivity is controlled by varying the active site density and the turnover rates characteristic of such sites. Supported Co catalysts with high specific rates require the synthesis of small metal crystallites at high local surface densities on support surfaces and the use of supports or alloy elements that increase the rate per surface Co atom (turnover rate).

At reaction conditions leading to the predominant formation of short paraffins (100 kPa, > 493 K), cobalt atoms at the surface of small crystallites appear to be less active for CO hydrogenation reactions than those in larger crystals [17,18]. Also, TiO<sub>2</sub> supports appear to lead to higher methanation turnover rates on several metals [19] than other supports, apparently because TiO<sub>x</sub> overlayers that form during reduction pretreatments influence CO and H<sub>2</sub> adsorption thermodynamics. These crystallite size and support effects are found in a range of crystallite sizes in which surface structure should not be very sensitive to crystal size [20,21], and where the number of Co atoms in contact with the support is a very small fraction of the total number of metal atoms in a crystal. Later studies have shown that these observed effects of crystallite size may be indirect. They appear to reflect the incomplete reduction of  $CoO_x$  precursors or the reoxidation of Co metal as water is formed in FTS reactions [18], both of which depend on Co crystallite size. Similarly, the formation of  $TiO_x$  overlayers, which increase methanation turnover rates by favoring the adsorption of hydrogen over CO, is rapidly reversed by the significant water concentrations present at useful FTS reactant pressures and conversions [3,8]. As we discuss below, the reversal of these  $TiO_r$ decoration processes may also be involved in the rate enhancements induced by the addition of water to low conversion FTS reactors and discussed in detail later in this review.

Turnover rates (site-time yields) are not influenced by dispersion or support effects at conditions favoring chain growth (C<sub>5+</sub> selectivity > 80%). At 2000 kPa, 473 K, and CO conversion levels above 30–40%, we observe that cobalt-time yields (mole CO converted/gatom total Co-s) increase linearly with increasing Co dispersion, irrespective of the chemical identity of the metal oxide support (Fig. 1), over the entire experimental dispersion range (0–0.12). Turnover rates vary between  $1.6 \times 10^{-2} \text{ s}^{-1}$  and  $3.0 \times 10^{-2} \text{ s}^{-1}$  for a series of Co catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>-modified TiO<sub>2</sub>, and MgCr<sub>2</sub>O<sub>4</sub> (Fig. 2).

These data show that FTS reactions do not detect the presence of any structural surface features that vary as dispersion changes within our experimental range or any electronic perturbations introduced by contact with a specific metal oxide support. These results suggest that Fischer-Tropsch synthesis is a structure-insensitive reaction by the definition of Boudart [20], although the experimental dispersion range is not sufficient to reach an unequivocal conclusion, because crystallite surface structure and orientation (and thus turnover rates) depend only weakly on crystallite diameter over this dispersion range [20,21]. Recent studies have shown that methanation turnover rates are also independent of Co dispersion on supported catalysts [18,22] and of surface orientation on Co single crystals and films [18,23].

An interesting type of support effect appears at low synthesis gas pressures (560 kPa), and at higher pres-



Fig. 1. Effect of cobalt dispersion (ratio of surface Co to total Co atoms), support, and alloying on FTS Co-time yields (moles CO converted/total g-atom Co-s) [tubular packed-bed reactor; reaction conditions: 473 K, 2000 kPa, H<sub>2</sub>/CO=2.05, 55–65% CO conversion, C<sub>5+</sub> selectivity >80%; 0.17 mm pellet size].

sures (2000 kPa) when CO conversions are low (<30%). At these conditions, turnover rates on TiO<sub>2</sub>-supported Co and on Co catalysts supported on large-pore, low surface area silicas  $(80 \text{ m}^2 \text{ g}^{-1})$ are significantly lower than on other supported Co catalysts (Fig. 3), but turnover rates reach values similar to those reported in Fig. 2 when water is added with the H<sub>2</sub>/CO reactants or when conversion is raised above 30-40% (Fig. 4). This autocatalytic effect of water leads to an increase in reaction rate as CO conversion increases, because of the concomitant increase in water concentration within the reactor (Fig. 4). At CO conversions above 30%, or when water is added to the H<sub>2</sub>/CO feed at lower conversions, turnover rate differences among samples disappear, as shown in Figs. 1 and 2.

Indigenous or added water initially increase FT synthesis rates and olefin and  $C_{5+}$  selectivity on Co/TiO<sub>2</sub> catalysts (Table 1, Fig. 4); at high enough water concentrations, such effects appear to 'saturate' and rates and selectivities are much more weakly affected by further increases in water concentration.



Fig. 2. Effect of cobalt dispersion (ratio of surface Co to total Co atoms), support, and alloying on FTS turnover rates (moles CO converted/surface g-atom Co-s) [tubular packed-bed reactor; reaction conditions: 473 K, 2000 kPa, H<sub>2</sub>/CO=2.05, 55–65% CO conversion,  $C_{5+}$  selectivity >80%; 0.17 mm pellet size].

 Table 1

 Effect of added water on FTS rate and selectivity

Avg. H <sub>2</sub> O pressure (kPa)	Site-time yield (10 <sup>2</sup> s <sup>-1</sup> )	Methane selectivity (%)	Propene/propane ratio
51	0.7	9.3	2.3
115	1.3	7.5	2.4
185	1.6	6.1	2.8
228	1.9	5.0	2.9
350	2.3	4.2	3.0
585	2.5	3.8	3.1
940	2.1	3.5	3.3

12.1% Co/TiO<sub>2</sub>, 0.058 dispersion, conditions as in Fig. 1, 8% CO conversion, no  $H_2O$  added for 51 kPa point.

Thus, it appears that at conditions typical of practical FTS operations (high pressure and CO conversion) support effects disappear, water concentration effects become 'saturated', and catalyst productivity can be predicted directly from Co dispersion values measured by hydrogen chemisorption.



Fig. 3. Effect of reactant pressure on FTS site-time yields (moles CO converted/surface g-atom Co-s) [Reaction conditions: 473 K,  $H_2/CO=2.05$ , 55–65% CO conversion,  $C_{5+}$  selectivity >80%; 0.17 mm pellet size].

The addition of water to  $H_2/CO$  reactants increases  $C_{5+}$  selectivity and reduces  $CH_4$  yields on  $Co/SiO_2$  [24],  $Co/TiO_2$  [25], and  $Co-Mg-Th-SiO_2$  [26] catalysts. The latter study also reports an increase in FTS rate and in olefin selectivity when water is added to the synthesis gas feed [25].  $C_{5+}$  selectivity increased and the  $CH_4$  selectivity decreased as the concentration of indigenous or added water increases in packed-bed FTS reactors [25].

The underlying processes responsible for these water effects remain unclear. The autocatalytic effects initially observed on  $TiO_2$  supports could be attributed to the reversal of decoration processes that occur during catalyst reduction and block Co surface atoms. Water effects, however, were also observed on some silica samples and even on Co powders, on which the inhibition of chemisorption uptakes with increasing reduction temperatures, typical of decorated metal crystals, was much weaker or did not occur. The removal of a catalyst impurity by water was also considered, but the concentration of trace elements on silica samples showing normal and autocatalytic



Fig. 4. Autocatalytic water effects on Co supported on  $TiO_2$ . Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. CO conversion effects on FTS turnover rates (site-time yields) [Conditions as in Fig. 1, conversion varied by changing bed residence time].

behavior were similar. Rate enhancements caused by water were fully reversible upon changes in water concentration.

The addition of water also increases the olefin content and  $C_{5+}$  selectivity of FTS products (Table 1). Water selectively inhibits irreversible chain termination by hydrogen addition and secondary hydrogenation pathways. Surface modifications by chemisorbed water are unlikely to be influenced by the identity of the support for the large Co crystallites of this study (>10 nm). Thus, it is difficult to explain how such chemical modifications of the surface could be influenced by support effects. An alternate explanation, which is discussed in Section 5, is that small-pore supports, such as Al<sub>2</sub>O<sub>3</sub> and small-pore SiO<sub>2</sub>, contain a separate intrapellet water phase, which facilitates CO and H<sub>2</sub> transport within the porous structure and increases the accessibility of isolated transport-limited regions within porous pellets. This condensed water phase would form only at much higher water partial pressures in larger-pore materials, such as TiO<sub>2</sub>, largepore SiO<sub>2</sub>, and low surface area Co powders.

#### 3. Synthesis of supported cobalt catalysts

The limited range of cobalt dispersion shown in the data of Figs. 1 and 2 reflects the significant synthetic hurdles that exist in the preparation of small Co metal crystallites on oxide supports. The synthesis of highly dispersed Co catalysts requires the initial formation of very small CoO or Co<sub>3</sub>O<sub>4</sub> crystallites. The formation of these small oxide clusters in turn requires strong interactions between the support and the Co precursor; such interactions tend to interfere with the low-temperature reduction of such precursors to Co metal [27]. On strongly interacting supports, high reduction temperatures are required and they lead to extensive agglomeration and to the formation of large Co metal particles. Cobalt precursors can be readily reduced on weakly interacting supports, but such supports are unable to stabilize very small precursor crystallites during impregnation and drying. Thus, optimum cobalt dispersions are favored by support-precursor combinations with intermediate interaction strength [27].

For example, alumina-cobalt nitrate and silicacobalt carboxylate support-precursor pairs lead to very small CoO<sub>x</sub> particles, which reduce completely only above 800 K and form sintered metal particles. Silicacobalt nitrate and MgCr<sub>2</sub>O<sub>4</sub>-cobalt nitrate pairs lead to CoO<sub>x</sub> particles of intermediate size during nitrate decomposition; these crystallites reduce at 573– 673 K without significant agglomeration, and lead to cobalt dispersions of 0.08–0.11. Co dispersions above 0.10 can also be achieved by using carbonyl precursors or by impregnation with concentrated nitrate solutions, followed by the direct reduction of nitrate precursors using slow temperature ramping protocols (Table 2) [16].

The procedures used for the decomposition and reduction of catalyst precursors also influence Co

Table 2

Pretreatment	effects on C	Co dispersion	n [13% wt.	Co/SiO <sub>2</sub> ,	impreg-
nated to inci	pient wetnes	s with Co ni	trate solution	on]	

Treatment	Co dispersion from hydrogen chemisorption
Air (673 K); $H_2$ (to 623 K at 4 K min <sup>-1</sup> )	0.030
$H_2$ (to 623 K at 4 K min <sup>-1</sup> )	0.057
$H_2$ (to 623 K at 0.2 K min <sup>-1</sup> )	0.118

metal dispersions for a given precursor-support pair. It appears that the exothermic decomposition of nitrate precursors and oxidation of CoO to Co<sub>3</sub>O<sub>4</sub> during oxidative treatments and the high H2O concentrations that develop during rapid reduction of oxides and nitrates by H<sub>2</sub> lead to agglomeration of Co particles and to low metal dispersion. The elimination of 'calcination' steps, by reducing nitrate precursors directly in flowing H<sub>2</sub>, increases Co dispersion from 0.030-0.057 (Table 2). In addition, the use of high  $H_2$  flow rates and slow temperature ramping protocols lead to additional improvements in cobalt dispersion to values above 0.10 (Table 2), even at high Co concentrations, such as those required in eggshell catalyst configurations described later [16]. Subsequent oxidationreduction cycles after initial reduction do not lead to detectable agglomeration of Co crystallites.

Cobalt dispersions above 0.15-0.20 (5–6 nm crystallite diameters) are difficult to achieve during synthesis; they are also difficult to maintain during periodic oxidative regenerations at high temperatures, which are ultimately required to remove deactivating deposits during long-term reactor operation. Also, small Co metal crystallites (<5–6 nm diameter) appear to reoxidize and deactivate rapidly in the presence of water reaction products at typical FTS conditions. Thus, it is unlikely that marked improvements in volumetric productivities can be achieved by increasing Co metal dispersions above 0.15. Instead, catalyst productivities can be increased significantly by the synthesis of materials with Co dispersions of 0.10–0.15 at higher cobalt concentrations (40–50% wt.).

The use of support-precursor pairs with intermediate interaction strengths and the slow and controlled reduction of impregnated precursors appear to be the most promising route to the synthesis of supported Co catalysts with high Co concentrations and modest dispersions (0.10-0.15). These methods have been used in the synthesis of eggshell catalysts, in which very high concentrations of Co are placed locally within the external regions of large catalyst pellets using cobalt nitrate melt precursors [16]. Co dispersions of 0.08-0.12 have been obtained at local Co concentrations above 50% wt. in these eggshell catalysts by using nitrate melts and their slow direct reduction in flowing H<sub>2</sub>. These synthesis techniques lead to very high volumetric Co site densities and FTS reaction rates. As we discuss in a later section, high

volumetric site densities also lead to high selectivity to desired  $C_{5+}$  products, because they favor the reversal of chain termination steps via diffusion-limited readsorption of  $\alpha$ -olefins.

#### 4. Alloy effects in cobalt-ruthenium and cobaltrhenium bimetallic catalysts

Catalyst productivity in FTS reactions can also be increased by combining Co with another metal in order to increase the number of exposed Co sites (structural promotion) or the FTS rate per exposed Co metal atom (chemical promotion). A second metal component in intimate contact with Co can increase the number of exposed Co atoms by modifying either the strength of  $CoO_x$ -support interactions or the reducibility of  $CoO_x$  precursors. For example, the addition of Ru to Co/Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub>, and Co/TiO<sub>2</sub> catalysts decreases the temperature at which  $CoO_x$  precursors reduce to Co metal [15]. This structural promotion requires intimate contact between Co and Ru components; such contact appears to require oxidation treatments that form mobile  $RuO_x$  species and thermodynamically stable Co-Ru mixed oxides. On Al<sub>2</sub>O<sub>3</sub>, the presence of Ru leads to higher apparent Co dispersions, because CoO and Co<sub>3</sub>O<sub>4</sub> crystallites strongly interacting with the alumina support are more easily reduced when Ru is present, as also reported by others [28]. These effects of Ru on  $CoO_x$  reduction are enhanced by reduction-oxidation cycles that promote bimetallic mixing [15,28]

Rhenium is also a structural promoter of supported Co catalysts, but it acts by preventing agglomeration of  $CoO_x$  particles during calcination treatments and oxidative regenerations [29–31]; Re leads to higher Co metal dispersions on TiO<sub>2</sub>, without influencing FTS turnover rates. The presence of Re (0.8% wt.) in Co/ TiO<sub>2</sub> leads to an increase in dispersion from 0.022– 0.053 (Fig. 1, open squares). This increase in dispersion disappears when catalysts are prepared by direct reduction of cobalt nitrate precursors without intervening oxidation at high temperatures. Re oxide species appear to anchor CoO<sub>x</sub> clusters or to decrease their 'volatility' and thus inhibit their migration and sintering in oxidizing environments.

A second element can also act as a chemical promoter and increase the turnover rate characteristic

of Co surface atoms in monometallic catalysts. The addition of very small amounts of Ru (Ru/Co = 0.0067 at.) increases FTS turnover rates on Co/SiO<sub>2</sub> and Co/TiO<sub>2</sub> catalysts (Fig. 1) [15]. On Co/ TiO<sub>2</sub>.(11.7% wt., Co; 0.022 dispersion), the addition of Ru increases turnover rates increase from 1.7  $\times$  $10^{-3}$  s<sup>-1</sup> to 5.6  $\times$   $10^{-3}$  s<sup>-1</sup>, without any apparent change in the cobalt dispersion measured on fresh catalysts or in the rate parameters (activation energy and reaction orders) observed on monometallic Co catalysts (Fig. 1). This apparent chemical promotion is enhanced by oxidative pretreatments above 573 K before catalytic reaction tests. In situ X-ray absorption measurements have shown that oxidation above 573 K increases the number of Co neighbors near Ru atoms in reduced crystallites, suggesting that the enhanced synergistic effects caused by oxidative treatments reflect better mixing of Co and Ru components during oxidation [15]. The reduction temperature of bimetallic oxide precursors decreases as the temperature of the oxidation treatment increase, also suggesting more intimate contact between Co and Ru after oxidation treatments [15]

The higher turnover rates observed on well-mixed Co–Ru crystallites cannot be explained by an additive contribution of surface Ru atoms to the FTS activity of the exposed surface Co atoms, even if all the added Ru atoms were exposed at the surface. First, turnover rates on Ru catalysts are similar or even slightly lower than on Co catalysts [3,7,8], suggesting that the replacement of a surface Co atom by Ru would make negligible contributions to the observed reaction rate. Also, an additive contribution should not require intimate mixing between the two components. Finally, the addition of Ru does not affect FTS reaction rate orders or activation energies, even though these kinetic properties are measurably different on monometallic Ru and Co catalysts [8].

The presence of Ru appears to preserve a larger fraction of the surface Co atoms available for catalytic reactions during FTS. The reported turnover rates are based on the initial dispersion of Co catalysts, because of the obvious difficulty in obtaining such measurements on liquid-filled catalysts pellets after reaction. The constant turnover rates shown in Fig. 2 for monometallic Co catalysts suggest that the fraction of surface Co atoms that remains available for reaction at steady-state is not influenced by support or dispersion effects. The higher turnover rates observed on Co–Ru catalysts may reflect a protective effect of the Ru component on the accessibility of reduced surface Co atoms, perhaps by inhibiting their oxidation or the deposition of carbon during FTS reactions.

These inhibited deactivation effects are consistent with thermogravimetric data and X-ray photoelectron spectra, which show that carbon deposition from H<sub>2</sub>/ CO mixtures occurs at higher temperatures when Ru is present and well-mixed with Co on Co/TiO2 catalysts and Co foils [15]. The presence of Ru may also facilitate the removal of surface oxygen during FTS reactions. CO dissociation elementary steps during FTS lead to the formation of surface oxygen and hydroxyl species that must be removed by reaction with H<sub>2</sub> to form the water product of the synthesis reaction. The presence of Ru is likely to increase the rate of this surface reduction reaction and to inhibit the surface and bulk oxidation of Co crystallites. These inhibited oxidation effects may increase the stability of cobalt catalysts during FTS, especially for small crystallites, at the high water concentrations typical of backmixed slurry reactors at high synthesis gas conversion levels.

## 5. Chain growth selectivity on supported cobalt catalysts

Chain growth selectivity depends on the size and composition of cobalt crystallites and on the chemical identity of the metal oxide support [3], an unexpected result in view of the constant site activity observed on these samples. For example, carbon number distributions on Co/Al<sub>2</sub>O<sub>3</sub> (19.5% wt. Co, 0.036 dispersion), Co/SiO<sub>2</sub> (24.8% wt., 0.042 dispersion), and Co/TiO<sub>2</sub> (11.8% wt., 0.022 dispersion) are significantly different (Fig. 5). Also, increasing the dispersion of Co crystallites on TiO<sub>2</sub> from 0.022-0.058 increases C<sub>5+</sub> selectivity from 85%-90.5% (Fig. 6) at about 50% CO conversion. A similar increase in  $C_{5+}$  selectivity is observed when Ru is added (Fig. 6). C<sub>5+</sub> selectivities on Ru catalysts are very similar to those measured on Co. Thus, this increase in  $C_{5+}$  selectivity cannot be explained by the presence of isolated Ru sites in Co-Ru bimetallic catalysts. The addition of Ru increases apparent turnover rates by a factor of three, without influencing the initial Co metal dispersion (Fig. 1).

Figs. 5 and 6 also illustrate two unusual but commonly observed features of chain growth selectivity in FTS reactions. The carbon number distributions do not obey Flory chain growth kinetics, which would lead to straight lines in the semi-logarithmic distribution plots of Fig. 5. Instead, the apparent chain growth probability increases with increasing chain size, leading to the curved semi-logarithmic plots of Fig. 5. Also, Fig. 6 shows an increase in  $C_{5+}$  selectivity as CO conversion is increased by increasing reactor residence time, suggesting that either secondary reactions contribute to chain growth or that one of the reaction products (e.g., H<sub>2</sub>O) increases chain growth probabilities and product molecular weight. As CO conversion increases, CH<sub>4</sub> selectivity decreases, the olefin content within each carbon number group decreases, but the chain growth probability for  $C_{15+}$  chains is only weakly influenced by bed residence time.

Termination probabilities for chains with *n* carbon atoms ( $\beta_{T,n}$ ) can be obtained from complete carbon number distributions using the formalism described in Scheme 2 and first proposed by Herrington [32]. The termination probability of C<sub>2</sub>–C<sub>15</sub> chains decreases with increasing bed residence time. Chain termination appears to slow down, or possibly be reversed, as bed residence time increases; termination also becomes less likely or more easily reversed for larger surface chains at a given bed residence time (Fig. 7). This latter effect leads to the non-Flory molecular weight distributions widely reported in the FTS literature and discussed in detail elsewhere [3,7].

#### 6. Chain growth reaction pathways and Fischer-Tropsch synthesis selectivity

Cobalt crystallites on non-acidic supports lead to the selective formation of  $\alpha$ -olefins and *n*-paraffins at the high CO pressures and conversions typical of industrial practice [3,7]. High CO and H<sub>2</sub>O partial pressure inhibit secondary hydrogenation and isomerization reactions on supported cobalt catalysts.

#### 6.1. Chain termination and readsorption of $\alpha$ -olefins

The readsorption of  $\alpha$ -olefins merely reverses the predominant chain termination pathways of small surface chains ( $\beta$ -hydrogen abstraction) by re-initiat-



Fig. 5. Support effects on carbon number distribution in supported cobalt catalysts. [0.17 mm pellet size; reaction conditions as in Fig. 1].

ing surface chains that continue to grow and ultimately desorb as larger hydrocarbons (Scheme 1). In effect, termination of alkyl chains via  $\beta$ -hydrogen abstraction becomes increasingly reversible as olefin concentration or residence time increase; this readsorption reaction also becomes faster as reactive olefins are retained longer within liquid-filled catalyst pellets. This well-known secondary reaction ([3] and references therein) leads to an increase in the selectivity to C<sub>5+</sub> hydrocarbons and to lower selectivities to CH<sub>4</sub> and olefins as bed residence time increases. Clearly, readsorption effects become more influential as olefin concentrations increase with increasing bed residence time and CO conversion.

The effects of bed residence time and of olefin addition to  $H_2/CO$  feeds confirm the significant role of olefin readsorption on chain termination pathways. Increasing bed residence time leads to a decrease in the selectivity to 1-butene, without a corresponding increase in the selectivity to *n*-butane or 2-butenes



Fig. 6. Site density and alloy effects on  $C_{5+}$  selectivity (Co/TiO<sub>2</sub>) [A: 11.7% Co, 0.022 dispersion (*d*), 10<sup>-6</sup> g-atom surface Co m<sup>-2</sup> ( $\theta_{Co}$ ); B: 12.1% Co, *d*=0.058,  $\theta_{Co}$ =3.3 × 10<sup>-6</sup>; C: 11.7% Co, (Ru/ Co)<sub>at</sub> =0.0067, d=0.024,  $\theta_{Co}$ =1.1×10<sup>-6</sup>] [0.17 mm pellets].

$$\beta_{T,n} = r_{t,n} / r_{p,n} = \phi_n / \sum_{n+1}^{\infty} \phi_i$$
  
$$\beta_{T,n} = \beta_{o,n} + \beta_{h,n}$$

#### $\phi_n = \text{molar rate of formation of chains}$ with n carbons

Scheme 2. Chain growth parameters in Fischer-Tropsch synthesis.

(Fig. 8). Thus, the depletion of  $\alpha$ -olefins, such as 1butene, from FTS products is not caused by secondary hydrogenation or double-bond migration reactions, but instead by the selective disappearance of 1-butene, caused by its re-attachment to the surface and subsequent chain growth. The decrease in olefin/paraffin ratios observed with increasing bed residence is also caused by selective readsorption steps (Fig. 9). Readsorption pathways remain available as long as chain growth is terminated by  $\beta$ -hydrogen abstraction, but they cannot occur again after chains terminate irreversibly as unreactive paraffins. Thus, the paraffin



Fig. 7. Bed residence time and carbon number effects on total chain termination probability. A: 9.5% CO conversion, 2 s bed residence time; B: 72% CO conversion, 12 s bed residence time [Co/TiO<sub>2</sub>, 11.7% Co, 0.015 dispersion, 0.17 mm pellet size; 473 K, 2000 kPa, H<sub>2</sub>/CO=2.1]

content in reaction products increases with increasing bed residence time, as FTS products become dominated by 'dead-end' n-paraffins, which cannot undergo surface reattachment and chain initiation because of unfavorable thermodynamics. Secondary hydrogenation reactions appear to be strongly inhibited by water and CO concentrations typical of FTS reactions [3], but these reactions can influence product selectivity at the low pressure and conversion conditions typical of many previous literature reports. As expected from the reaction pathways (Scheme 1) and the definition of chain termination probability (Scheme 2), higher extents of readsorption for larger chains and at long residence time appear to be related to the low chain termination probabilities observed for these products and reaction conditions.

These bed residence time studies show that  $\alpha$ olefins initiate surface chains with very high selectivity, even though  $\alpha$ -olefins added to H<sub>2</sub>/CO feeds undergo significant hydrogenation (Table 3). Added olefins hydrogenate predominantly at the dry conditions of the reactor inlet, but the water product of FTS reactions strongly inhibits the hydrogenation of olefins



Fig. 8. Bed residence time effects on olefin and paraffin selectivity within  $C_4$  products on Co/TiO<sub>2</sub> (catalyst: 11.7% wt. Co, 0.015 dispersion, 9.5–72% CO conversion; reaction conditions as in Fig. 1; selectivity reported on a carbon basis as the percentage of the converted CO appearing as a given product).

Table 3

Hydrogenation and chain initiation reactions of ethylene during FTS [11.7% Co/TiO<sub>2</sub>, 0.017 dispersion, 2070 kPa, <15% CO conversion, 8% mol  $C_2H_4$  in feed,  $H_2/CO=2.1$ ] [9]

Hydrogenation (%)	Chain initiation (%)	
70.5	29.5	
15.1	84.9	
31.5	68.5	
22.0	78.0	
	Hydrogenation (%) 70.5 15.1 31.5 22.0	

formed (along with water) by FTS reactions. The presence of water in the  $H_2/CO$  feed or the external introduction of olefins below the 'dry' reactor inlet markedly increase the chain initiation selectivity of added olefins (Table 3). Previous olefin addition stu-

dies of the role of readsorption pathways were carried out at low pressures and 'dry' conditions. As a result, these studies have significantly underestimated the critical role of these chain initiation pathways in the control of carbon number distributions in FTS reactions.

The total chain termination probabilities obtained from the approach described in Scheme 2 ( $\beta_{T,n}$ , Fig. 7) can be separated into individual termination probabilities for the two predominant termination steps: hydrogen addition ( $\beta_{h,n}$ ) and hydrogen abstraction ( $\beta_{0, n}$ ) (Figs. 10 and 11). In effect, the contributions of the two termination pathways to the formation of hydrocarbons of a given length can be obtained from the complete carbon number distribution and the olefin/ paraffin content for each chain length (Scheme 2). A similar separation is not possible with the normally



Fig. 9. Bed residence time and carbon number effects on  $\alpha$ -olefin to *n*-paraffin ratio on Co/TiO<sub>2</sub> [Catalyst and reaction conditions as in Fig. 8]

reported values of chain growth probability  $(r_p/r_t)$ , because the additive chain termination rates appear in the denominator.

The net probability of chain termination to olefins decreases with increasing chain length, but the probability of termination to paraffins is independent of chain size (Fig. 10). Therefore, the decrease in total chain termination probability with chain size (Fig. 7) and the non-Flory carbon number distributions (Fig. 5) reflect a selective decrease in the net rate of chain termination to olefins, without any apparent influence of chain size on the irreversible H-addition termination step that forms paraffins (Fig. 10). The higher  $C_{5+}$  selectivity and paraffin content obtained at long bed residence times is caused by a decrease in the net rate of chain termination to olefins, without significant changes in the rate of chain termination to paraffins, as shown by a comparison of the chain termination probabilities at short (Fig. 10; 2 s) and long (Fig. 11; 12 s) residence times.

It appears unlikely that the forward rate of chain termination to olefins ( $\beta$ -hydrogen abstraction) would depend strongly on chain length, in view of the chain size independent termination rate for the irreversible hydrogen addition step and of the observed effect of bed residence time on the calculated probability of termination to olefins. The results reported here strongly suggest that the observed decrease in the net olefin termination probability reflects the higher probability of reversing the  $\beta$ -hydrogen abstraction step by readsorption as the size of hydrocarbon chains increase. This higher probability in turn reflects the slower diffusivity and the generally higher reactivity of larger olefins, both of which lead to more severe



Fig. 10. Chain size effects on termination probabilities to olefins and paraffins [9.5% CO conversion, 2 s bed residence time; Co/TiO<sub>2</sub>, 11.7% Co, 0.015 dispersion, 0.17 mm pellet size; 473 K, 2000 kPa, H<sub>2</sub>/CO=2.1]

diffusional restrictions within liquid-filled pores as chain length increases [3]. This proposal, however, must also be able to account for the otherwise unexplained effects of alloying, dispersion, and support identity on FTS selectivity (Figs. 5 and 6). Indeed, the severity of diffusional restrictions is typically controlled by varying the volumetric density of active sites and the diameter and pore structure of support pellets.

# 6.2. Diffusion-enhanced chain growth and site density effects on selectivity

Rigorous mathematical descriptions of diffusional transport within catalyst pellets and of chain growth and termination surface kinetics have led to excellent agreement with experimental measurements of chain termination probabilities [3,7]. For example, the curves shown along with the experimental data in Fig. 10 were obtained from simulations using these reaction-transport models [3,7] and a chain length dependence only for the diffusivity and the readsorption rate constant of olefins with n carbon atoms:

$$(D_n/k_{r,n}) = (D_6/k_{r,6})\exp[-\gamma(n-6)].$$
 (1)

This exponential dependence includes chain size effects on olefin diffusivity  $(D_n)$  and reactivity  $(k_{r,n})$  from independently obtained values for 1-hexene and a value of  $\gamma(0.29)$  adjusted to match the experimental results in Fig. 4.

Dimensional analysis of the boundary value problem posed by a reaction-diffusion mole balance for



Fig. 11. Chain size effects on termination probabilities to olefins and paraffins [72% CO conversion, 12 s bed residence time; Co/TiO<sub>2</sub>, 11.7% Co, 0.015 dispersion, 0.17 mm pellet size; 473 K, 2000 kPa, H<sub>2</sub>/CO=2.1]

each hydrocarbon chain within a catalyst pellet shows that diffusional restrictions depend on a dimensionless parameter  $\Phi_n$ , which reflects the ratio of maximum diffusion rates to maximum reaction rates for an  $\alpha$ -olefin with *n* carbon atoms:

$$\Phi_n = (k_{r,n}/D_n) \times (R_o^2 \varepsilon \theta_{\rm Co}/r_{\rm p}) = (\psi_n) \times (\chi)$$
(2)

The severity of transport restrictions, and the extent to which these restrictions enhance the probability of olefin readsorption, increase as the value of  $\Phi_n$  increases.

The first term  $(\psi_n)$  in Eq. (2) contains a first-order rate constant for olefin readsorption reactions  $(k_{r,n})$ and the effective diffusivity  $(D_n)$  of an  $\alpha$ -olefin within a catalyst pellet. This term reflects predominantly the molecular properties of olefins with *n* carbon atoms and leads to the observed effect of chain size on termination probability and olefin content (Figs. 3 and 4). This  $\psi_n$  term is only weakly affected by the support pore structure within the narrow range of void fraction and tortuosity typical of the type of supports used in this study.

The second term  $(\chi)$  in Eq. (2) contains the average radius of catalyst pellets  $(R_0)$  the density of Co sites per unit area  $(\theta_{Co})$ , and the void fraction  $(\varepsilon)$  and average pore radius  $(r_p)$  of the metal oxide support. The last three catalyst properties appear as a combined term  $(\varepsilon \theta_{Co}/r_p)$ , which is proportional to the volumetric density of surface Co atoms (Co surface atoms per unit pellet volume). This structural term  $(\chi)$  contains structural catalyst properties that can be independently measured and it appears in the  $\Phi_n$  term for all values of *n*. The structural parameter  $\chi$  term depends only on the number of sites available for chain desorption and readsorption and on the average distance that molecules must traverse by diffusion within the *intrapellet* liquid phase before they are removed by convective gas flow within *intrapellet* bed interstices.

The effects of catalyst structure and site density suggested by the parameter  $\chi$  give rise to an increase in the extent of readsorption and in  $C_{5+}$  selectivity as Co site density is increased either by increasing Co loading or dispersion in monometallic catalysts or by maintaining a larger fraction of the exposed Co surface atoms available during steadystate FTS in Co-Ru catalysts (Figs. 5 and 6). Chain termination probabilities decrease with increasing site density (at least on small pellets) because termination to olefins is more likely to be reversed when diffusional restrictions increase intrapellet olefin concentrations and lengthen intrapellet residence times. The resulting changes in  $C_{5+}$  selectivity occur without any changes in the asymptotic chain growth probability, which reflects the intrinsic rate of the irreversible hydrogen addition termination step. Therefore, the kinetics of intrinsic chain growth and termination do not need to be influenced by changes in Co dispersion or support structure in order to account for their observed effects on olefin content, carbon number distribution, and  $C_{5+}$ selectivity.

Carbon number and olefin selectivity changes caused by dispersion, support, and alloy effects can also be described by the effects of site density and support structure on the rate of diffusion-enhanced olefin readsorption reactions. A rigorous comparison of the predicted and observed selectivity changes induced by variations in the parameter  $\chi$  is shown in Fig. 12(a) and (b) for C<sub>5+</sub> and CH<sub>4</sub> selectivities, respectively.

For small values of  $\chi$ , the selectivity to C<sub>5+</sub> products increases (Fig. 12(a)) and methane selectivity decreases (Fig. 12(b)) as  $\chi$  increases, because diffusional restrictions decrease chain termination probabilities and increase average chain size. Fig. 12 includes Co, Co–Ru, and Co–Re catalysts of varying dispersion supported on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub>. The broken curves in Fig. 12 were obtained using identical



Fig. 12. The effect of structural parameters ( $\chi$ ) on Fischer-Tropsch synthesis selectivity: diffusion-enhanced readsorption (----) and diffusion-inhibited chain growth (----) simulations and experimental data ( $\bigcirc$ , dispersion/support effects;  $\blacktriangle$ , pellet size variations;  $\bullet$ , eggshell thickness variations: (a) C<sub>5+</sub> selectivity; (b) CH<sub>4</sub> selectivity [473 K, 2000 kPa, H<sub>2</sub>/CO=2.1, 55-65% CO conversion] ( $\chi$  values from Eq. (2), with  $r_p$  and  $R_o$  in *m* and  $\theta_{Co}$  in surface Co atoms m<sup>-2</sup>) [3,16].

values of chain growth kinetics, desorption rate constants, and olefin diffusivities for all catalysts.

Selectivity modifications caused by alloying, support, or dispersion changes reflect the indirect effect of these properties on diffusion-enhanced  $\alpha$ -olefin readsorption. Dispersion, support, and bimetallic effects do not influence the intrinsic chain growth properties of Co surfaces, at least in the experimentally accessible dispersion range; this conclusion is consistent with the observed structure insensitivity of CO hydrogenation reactions (Figs. 1 and 2). Excellent agreement between experiments and simulations can be obtained without varying the nature of the surface chain growth kinetics or introducing a carbon number dependence on intrinsic chain termination rates. Thus, intrinsic chain termination kinetics need not depend on carbon number, surface structure, or support modifications in order to explain non-Flory carbon number distributions (Fig. 5) or the observed effect of site density and pore structure on carbon number and olefin selectivities (Fig. 6). Clearly, diffusionenhanced  $\alpha$ -olefin readsorption processes cannot explain the decrease in product molecular weight that ultimately occurs at values of  $\chi$  above 200  $\times$  $10^{16} \text{ m}^{-1}$ . These simulations predict that C<sub>5+</sub> selectivities would reach an asymptotic value of about 92% as all olefins disappear from the effluent stream at very high values of  $\chi$ . In the next section, we show that diffusion-limited arrival of CO monomer precursors decrease chain growth probabilities and product molecular weight in large catalyst pellets and lead to the low  $C_{5+}$  selectivities observed on catalysts with high  $\chi$  values.

Recently, non-Flory distributions have been incorrectly attributed to the higher solubility of larger  $\alpha$ olefins within intrapellet and interpellet liquids in three phase reactors [33–35]; these authors proposed that this higher solubility leads to a selective increase in the concentration of heavier olefins, in their reactor residence time, and in the rate and extent of their secondary hydrogenation [33–35]. These proposals correctly assume that vapor–liquid equilibrium favors the presence of larger olefins in FTS liquids, but incorrectly conclude that such higher concentrations lead to faster readsorption rates. Chemical reactions, whether catalytic or not, are driven by the chemical potential of reactants. For a given reactant species, its chemical potential is identical in two or more phases, as long as these phases co-exist in thermodynamic equilibrium. In the absence of transport limitations, which would prevent attainment of thermodynamic equilibrium between phases, the rate of a chemical reaction cannot depend on the identity of the phase in which the catalyst resides or on the solubility of the reactants in this phase. Also, in three-phase reactors, the residence time of any products removed predominantly in the gas phase ( $C_1-C_{20}$ ) is controlled exclusively by gas phase residence time and the reactor gas hold-up as long as vapor-liquid equilibrium is maintained. Thus, a liquid phase holdup of higher olefins in the  $C_2-C_{20}$  range cannot explain the observed carbon number effects in the absence of transport limitations.

Olefin readsorption rates depend only on the olefin thermodynamic activity (not its concentration), which at vapor-liquid equilibrium is identical in the liquid and gas phases and independent of solubility at steadystate. The rate of readsorption depends only on the gas phase olefin fugacity, unless olefin partitioning between the gas and liquid phases is restricted by slow diffusion rates. In our model, a transport restriction in the removal of olefins leads to intrapellet olefin fugacities higher than in the interpellet gas phase; these fugacity gradients increase with increasing chain size because transport restrictions become more severe. In effect, a chemical reaction cannot 'detect' the presence of a liquid phase unless the liquid phase introduces either a transport restriction or a change in the reactive properties of the catalytic surface. Solubility-enhanced olefin readsorption, even if it were consistent with thermodynamics, cannot account for the observed effects of site density and pellet size on selectivity, because neither catalyst property can influence in any way vapor-liquid equilibrium.

At very high conversions or on catalysts with significant numbers of secondary hydrogenation or double-bond isomerization sites, reaction products approach Flory carbon number distributions. These secondary reactions convert  $\alpha$ -olefins into species with much lower readsorption rates and thus minimize readsorption events that cause changes in growth probability with chain size.

#### 6.3. Diffusion-inhibited chain growth

The selectivity trends caused by diffusion-enhanced olefin readsorption are ultimately reversed as transport

restrictions become more severe (Fig. 12), leading to a decrease in product molecular weight as  $\chi$  increases above  $200 \times 10^{16}$  m<sup>-1</sup>. Large pellets and high Co site densities inhibit chain growth, because they lead to significant depletion of monomer precursors (CO) within intrapellet liquids and on catalytic surfaces. Intrapellet gradients in the thermodynamic activity of CO arise when diffusion rates cannot satisfy the kinetic rate of CO hydrogenation reactions, either because of the distance CO must traverse or the number of sites that must be supplied with reactants per unit pellet volume. Chain termination probabilities  $(r_t/r_p)$  increase as  $\chi$  increases above a threshold value, because diffusional restrictions inhibit chain growth steps by reducing the supply of monomer species required for chain growth. A dimensional analysis of the reaction-diffusion equations for the CO hydrogenation steps shows that the severity of CO diffusional restrictions depends on a dimensionless parameter  $\Phi_{co}$  that accounts for the relative rates of CO diffusion and hydrogenation:

$$\Phi_{\rm CO} = (\psi_{\rm CO}) \times (R_{\rm o}^2 \varepsilon \theta_{\rm Co} / r_{\rm p}) = (\psi_{\rm CO}) \times (\chi), \qquad (3)$$

where  $\psi_{CO}$  is a function of the CO hydrogenation rate constant and the intrapellet CO diffusivity and  $\chi$  is identical to the structural parameter derived from the readsorption-transport equations for  $\alpha$ -olefins. The solid curves in Fig. 12(a) and (b) show the result of simulations using CO hydrogenation rate expressions obtained from kinetic-limited measurements and independently measured values for the H<sub>2</sub> and CO diffusivities and solubilities in FTS liquid products [3,7,16]. These simulations are in excellent agreement with experimental results for large values of  $\chi$ . Fortunately, the onset of CO transport restrictions occurs for  $\chi$  values significantly above those required in order to enhance olefin readsorption rates, because CO diffuses through intrapellet liquids much more rapidly than large olefins ( $\psi_{CO} << \psi_n$ ). Very few olefins remain in the product stream for  $\chi$  values leading to maximum  $C_{5+}$  selectivities, suggesting that the full benefit of olefin readsorption can be achieved before CO depletion begins to inhibit chain growth.

At this point, we reconsider the observed effects of water on FTS rate and selectivity in the context of the reaction-transport models just discussed. In particular, we observe that the effects of water on rate and selectivity mimic those predicted by the removal of reactant transport restrictions that can inhibit chain growth. CO transport restrictions decrease reaction rates, after an initial increase for modest transport restrictions (because of the negative order CO dependence of the reaction rate at high CO concentrations), by limiting the accessibility of sites near the center of large pellets. The lower intrapellet CO fugacities decrease chain growth probability and favor secondary hydrogenation of  $\alpha$ -olefins and preferential termination by hydrogen addition. The presence of water has directly opposite effects; it increases reaction rates (at least on some catalysts),  $C_{5+}$  and olefin selectivity, and chain growth probabilities of light hydrocarbon chains. Thus, we consider the possibility that the presence of water enhances the rate of transport of CO and H<sub>2</sub> reactants and increases the accessibility of sites located within the least accessible porous regions of catalyst pellets.

CO and H<sub>2</sub> diffusion coefficients are about three times larger in water than in typical FT hydrocarbon liquids [36,37]. Capillary effects can lead to the condensation of a separate water phase within catalyst pores, or to the formation of a hydrocarbon-water emulsion stabilized by minor alcohol components among FTS products, at concentrations well below the saturation vapor pressure of water at reaction conditions. Also, diffusional restrictions in the removal of the water formed in FT synthesis can lead to significantly higher water fugacities near the center of catalysts pellets than in the interpellet gas phase. Transport restrictions lead to intrapellet water gradients in the same range of  $\chi$  as required for CO gradients, because one water molecule is formed for each CO consumed and diffusion coefficients are similar for these two species. Preliminary simulation results suggest that the presence of a water or waterrich phase within intrapellet voids increases FT synthesis rates and  $C_{5+}$  and olefin selectivities [38]. Also, the slight model overprediction of CH<sub>4</sub> selectivity at high values of  $\chi$  (Fig. 12) may reflect the failure to include water concentration gradients in the simulations. Thus, one possible explanation for the autocatalytic and selectivity effects of water is that it enhances the rate of CO and H<sub>2</sub> diffusion within intrapellet liquids and removes deleterious diffusional effects affecting a minority of Co sites, which, however, form methane and light paraffins with high selectivity. If correct, this proposal would predict that

water can act as an indigenous moderator of CO diffusional restrictions in FT synthesis.

This simple proposal, however, seems to contradict the observation that water effects appear to be stronger on large-pore materials, in which capillary condensation is least likely to occur. This apparent contradiction can be resolved by considering that smallpore materials may already contain a separate water phase or a water-hydrocarbon emulsion, even at low water concentrations. Thus, these materials do not require high water concentrations in order to form a water-rich intrapellet liquid phase that makes internal pellet regions more accessible to reactants. Pellets with larger pores would form a water-rich phase only at higher water partial pressures, because of the weaker capillary effects expected within such larger pores. Independent evidence for this proposal or alternate explanations for these water effects are still needed. This two-phase model of intrapellet liquids, however, appears to provide the most reasonable explanation for the observed role of support pore size on the autocatalytic and selectivity effects of water during FTS reactions at this time. An alternate explanation involving reversible decoration of Co surfaces by reducible support species cannot account for the water effects observed on Co/SiO<sub>2</sub> catalysts, but may account for the effect of water on Co/TiO2 catalysts. In this case, indigenous or added water can reverse the blocking of Co surface atoms by re-oxidizing  $TiO_x$ species responsible for these decoration phenomena.

# 7. Optimum $C_{5+}$ selectivity and catalyst and reactor design options in the Fischer-Tropsch synthesis

The experimental and simulation results shown in Fig. 12 suggest that optimum  $C_{5+}$  selectivities (>90%) are obtained on FTS catalysts with intermediate values of the structural parameter  $\chi$ . The physical structure and the Co site density in FTS catalysts can be designed and constructed in a way that leads to desired carbon number distributions and olefin content in products. None of these design variables influences FTS selectivity on kinetic-limited catalyst pellets, because intrinsic chain growth probabilities and hydrogen addition and abstraction rates appear to be independent of surface structure and of bimetallic

composition on supported Co catalysts. Thus, transport restrictions introduce catalyst design variables that are not available in kinetic-limited catalysts. For example, light olefins are favored at very low  $\chi$  values, while light paraffins are formed preferentially at very high values of  $\chi$ . Intermediate  $\chi$  values lead to heavy paraffins and minimize the formation of light products.

Reactor and economic constraints determine the range of volumetric site densities (productivity) and pellet size (pressure drop in packed beds). These practical considerations may limit the range of  $\chi$  values that can be achieved using uniformly impregnated pellets in the packed-bed reactors used throughout most of experimental studies described in this review. For example, pressure drop constraints may require the use of large catalyst pellets (1–2 mm diameter), for which optimum values of  $\chi$  can only be obtained at very low site densities (and volumetric productivities).

In such instances, the use of pellets with Co sites preferentially located near the outer pellet surface allows the characteristic diffusion length to be varied independently of pellet diameter [16,39,40]. The relevant structural factor for such eggshell pellets becomes:

$$\chi = (\delta_{\rm o}^2 \varepsilon \theta_{\rm Co} / r_{\rm p}), \tag{4}$$

where  $\delta_0$  is the thickness of the eggshell layer [3,16]. The open symbols included in Fig. 12 show the experimental results obtained using eggshell pellets of varying eggshell thickness. These data illustrate the remarkable flexibility introduced by eggshell configurations in the design of FTS catalysts. The open symbol to the extreme right corresponds to a uniformly impregnated large SiO<sub>2</sub> pellet (2.2 mm diameter); the right to left sequence of open symbols shows how decreasing the eggshell thickness within such large pellets markedly increases C5+ selectivity and minimizes the formation of  $CH_4$  [3,16], without a significant decrease in volumetric catalyst productivity. High productivity can be achieved, in spite of the much smaller support volume and surface area onto which Co sites must be introduced, by using precursor-support pairs with intermediate interaction strength and by decomposing Co nitrate precursors slowly in flowing H<sub>2</sub>. Slow reduction of nitrate precursors on SiO<sub>2</sub> leads to Co dispersions of 0.08-0.12 even at local Co concentrations of about 50% wt. within the eggshell regions [16].

Eggshell catalysts are useful in packed-bed reactors, in which volumetric productivity and pressure drop constraints require the use of pellets with high  $\chi$ values. Slurry bubble column reactors contain much smaller catalyst pellets and typical  $\chi$  values tend to be lower than optimum values. Bubble column reactors require pellets that are small enough to ensure complete fluidization at economical linear velocities, but large enough to be easily separated from liquid reaction products. This imposes a fairly narrow range of pellet diameters, usually between 0.01 and 0.1 mm, for practical operation of bubble column reactors [41]. In this pellet size range, optimum values of  $\chi$  will require the selective deposition of high Co site densities near the pellet center or a significant increase in the site density and volumetric productivity of uniformly impregnated pellets. The latter approach is preferred because it also increases reactor productivity; it requires, however, the synthesis of high-loading supported Co catalysts with high Co dispersion (>10%). Slurry liquids that inhibit olefin diffusion also increase values of  $\psi_n$  Eq. (2) and can be used to compensate for the low values of  $\chi$  typical of small catalyst particles in slurry bubble column reactors.

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