Diffusion Limitations in Fischer-Tropsch Catalysts

The extent of diffusion limitations in the catalytic conversion of synthesis gas to hydrocarbons by the Fischer-Tropsch reaction has been established for a number of iron- and cobalt-based catalysts. The studies were performed in a fixed-bed microreactor system at temperatures in the range 473-523 K. Variation of catalyst particle size in the range 0.2-2.6 mm shows that the conversion of synthesis gas decreases considerably when the average particle size is increased. The effects of variation of particle size and pore diameter have been quantified with the Thiele model for diffusion limitations. Evidence has accumulated that the limited mobility of reactant molecules in the liquid-filled pores of Fischer-Tropsch catalysts is the main cause of retardation of the reaction rates. The experimentally determined reaction rates with various catalysts operated under different conditions show an excellent fit with the theoretical model.

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Introduction

In indirect conversion of natural resources such as coal, heavy oil, or natural gas into transportation fuels or chemicals, the first stage involves production of carbon monoxide and hydrogen (synthesis gas); subsequently, the desired products are synthesized via, for example, the Fischer-Tropsch (FT) reaction. Iron- and cobalt-based catalysts are known to be very effective FT catalysts for the synthesis of long-chain hydrocarbons from synthesis gas. The FT reaction is highly exothermic and much attention has therefore been paid to reactor selection, with emphasis on the ease of heat removal. The various types of reactors which have been considered (fixed-bed, fluidized-bed, ebulliating-bed, and slurry-phase) differ with respect to the most suitable particle size of the catalyst used.

If a fixed-bed mode of operation is envisaged, the FT catalyst will generally, for reasons of pressure drop and heat transfer, consist of particles of a few millimeters in size. It can be easily envisaged that, in catalyst particles of this size, intraparticle pore-diffusion limitations may prevail. Indeed, the existence of diffusion limitations inside catalyst particles has been reported (Anderson et al., 1952; Jacobs and Van Wouwe, 1982; Lox, 1987; Lucchesi et al., 1983) but the evidence is in general of a qualitative nature and is rather limited compared to the abundance of literature available on other aspects of the FT process. Some of the most pertinent information can be found in the results obtained by Anderson et al. (1952), who have demonstrated that the synthesis rate over a fused iron catalyst, which is essentially nonporous in the oxidic state, increases with decreasing particle size. This could be due to limitation of diffusion during the synthesis reaction (i.e., by the limited mobility of the reactants or the heavy hydrocarbon molecules, which would account for the significance of particle size), or to the activation of the nonporous oxidic catalyst particles being limited to a superficial layer only. In a recent study with a precipitation-type iron-based FT catalyst (Lox, 1987), such as is used in the commercial ARGE process, the occurrence of concentration gradients of synthesis gas in larger particles of this porous catalyst has been predicted on theoretical grounds; the experimental data, however, did not permit quantitative interpretation of the particle-size effects observed.

In order to establish, unequivocally, the existence of intraparticle pore-diffusion limitation in porous FT catalysts and to describe its effect in quantitative terms, we have conducted a study with a number of iron and cobalt catalysts, in which we have evaluated the effects of catalyst particle size and pore diameter on rates of carbon monoxide and hydrogen conversion. In this study, the kinetics of synthesis gas conversion was described by a simple but appropriate rate equation, while the well-known Thiele model was used to describe the effect of retardation of synthesis rates by intraparticle mass-transport limitations: see, for example, Froment and Bisschoff (1979),

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Satterfield and Sherwood (1963), and Weisz and Prater (1954).

Experimental

Catalysts

Table 1 constitutes a survey of the compositions and the relevant physical properties of the catalysts studied in this work. The catalytic materials are representative of five different types of FT catalyst, viz:

- A precipitated iron catalyst promoted with copper and sodium, sample 1
- An iron catalyst prepared by impregnation on porous silica and promoted with copper and potassium, sample 2
- A cobalt catalyst prepared by impregnation on porous alumina and containing the classical FT promoters, magnesium and thorium, sample 3
- A cobalt catalyst prepared by impregnation on porous silica and promoted with magnesium and thorium, sample 4
- Cobalt catalysts supported on porous silica of different particle sizes and pore diameters, promoted with zirconium, samples 5–8.

The porous texture of the catalysts in their oxidic form was determined by mercury intrusion porosimetry. The average pore diameter spanned the range 10–220 nm. Catalyst samples having the same compositions and porous textures but with different particle sizes were obtained either by grinding the parent catalyst (full size beads) and sieving the crushed material to the required size fraction, or by starting from carrier material of different particle size.

It was not possible to determine the porous texture of the catalysts in their reduced form, owing to their generally pyrophoric nature. In the case of catalysts prepared by impregnation of an inert carrier, it was assumed that the porous texture of the oxidic form would be very similar to that of the reduced catalyst.

Reactor system

Catalyst performance was studied in a standard fixed-bed microflow reactor (ID 9 mm) in downflow operation. The inventory of the catalyst samples having the largest particle size was normally kept at 5 mL. In all other cases, the catalyst charge was determined by weighing an amount of catalyst corresponding to 5 mL settled volume of the parent (large-particle) catalyst so as to eliminate the possibility of errors arising from differences in bed porosity. All catalysts were diluted with 20–50 mL silicon carbide particles (0.2 mm dia.) in order to maintain isothermal operation. The silicon carbide used, proved to be essentially inert under the conditions applied.

Catalyst activation and start-up

Catalyst activation was carried out *in situ* by a reductive treatment with a hydrogen/nitrogen mixture at 523 K. Subsequently, the catalyst was cooled under a stream of nitrogen to the desired start-of-run temperature, then pressurized with nitrogen prior to cutting in synthesis gas.

Results

Iron catalysts

The effect of catalyst particle diameter on the activity of the iron catalysts prepared by precipitation (catalyst 1) and by impregnation (catalyst 2) is summarized in the upper part of Table 2. The results show that conversion of synthesis gas and catalyst productivity (expressed as space-time yield) increase when the average catalyst particle size is decreased from about 2 mm, to less than 1 mm. This may be an indication that intraparticle diffusion substantially limits the rate of reaction in normal fixed-bed operation with 2–3 mm particles of this type of catalyst. The particle-size effect seems to be more pronounced with the catalyst prepared by precipitation, which will have a signifi-

Table 1. Survey of Catalysts Used

Sample No.	Nominal Composition, *pbw*	Avg.* Pore Dia. nm	Avg.* Part. Dia. mm	Origin**
1A	100 Fe/4.43 Cu/3.95 Na/20.5 SiO_2	†	2.1	
1B	100 Fe/4.43 Cu/3.95 Na/20.5 SiO_2	†	0.64	*c*
1C	100 Fe/4.43 Cu/3.95 Na/20.5 SiO_2	†	0.22	*c*
2A	25 Fe/1.25 Cu/1 K/100 SiO_2	220	2.2	*p*
2B	25 Fe/1.25 Cu/1 K/100 SiO_2	220	0.64	*c*
3A	25 Co/1.04 Th/1.18 Mg/100 Al_2O_3	15	2.3	*p*
3B	25 Co/1.04 Th/1.18 Mg/100 Al_2O_3	15	0.22	*c*
4A	25 Co/1.04 Th/1.18 Mg/100 SiO_2	100	2.3	*p*
4B	25 Co/1.04 Th/1.18 Mg/100 SiO_2	100	0.22	*c*
5	25 Co/0.9 Zr/100 SiO_2	150	0.38	
6A	10 Co/18 Zr/100 SiO_2	50	2.4	*p*
6B	10 Co/18 Zr/100 SiO_2	65	1.4	*p*
6C	10 Co/18 Zr/100 SiO_2	50	0.38	*c*
7A	25 Co/0.9 Zr/100 SiO_2	10	2.4	*p*
7B	25 Co/0.9 Zr/100 SiO_2	10	0.75	*c*
7C	25 Co/0.9 Zr/100 SiO_2	10	0.38	*c*
8A	25 Co/12 Zr/100 SiO_2	15	2.6	*p*
8B	25 Co/12 Zr/100 SiO_2	15	0.38	*c*

*Oxidic catalyst
***c* obtained by crushing catalyst, A; *p* prepared on preformed catalyst support particles
†Not determined on oxidic catalyst because porous texture changes upon reduction

Table 2. Effect of Catalyst Particle Size on Activity in Synthesis Gas Conversion*

Catalyst		Reaction Conditions			Catalyst Performance		
Sample No.	Particle Dia. mm	T K	GHSV	Feed Ratio mol/mol (H_2/CO)	Conv. % mol ($H_2 + CO$)	Space-Time Yield kg $C_{1+}/(m^3\ cat \cdot h)$	Growth Chance α
1A	2.1	493	1,000	2	30	62	—
1B	0.64	493	1,000	2	46	97	—
1C	0.22	493	1,000	2	52	104	—
2A	2.2	493	1,000	2	17	35	—
2A	2.2	523	1,000	1	38	80	—
2B	0.64	493	1,000	2	20	42	—
2B	0.64	523	1,000	1	50	105	—
3A	2.3	523	1,000	1	50	105	0.84
3B	0.22	523	2,000	1	55	230	0.85
4A	2.3	523	1,000	1	50	105	0.84
4B	0.22	523	2,000	1	55	230	—

*Pressure = 3.1 MPa

cantly lower porosity and average pore diameter, than the catalyst prepared by impregnation.

Cobalt catalysts promoted with magnesium and thorium

The lower part of Table 2 shows the results obtained with the title catalyst, supported either on a narrow-pore alumina (catalyst 3) or on a wide-pore silica (catalyst 4). Catalyst productivity benefits greatly from a decrease in particle size, while the selectivity (expressed as the growth chance, α, of the hydrocarbon product) is virtually unchanged. Catalyst performance appears to be virtually independent of type of carrier and pore diameter.

Cobalt-on-silica catalysts promoted with zirconium

An in-depth study of possible intraparticle diffusional effects was carried out with zirconium-promoted cobalt catalysts prepared by impregnation on porous preshaped silica spheres of different particle sizes and pore dimensions (catalysts 6, 7, and 8). The absence of significant diffusion limitations due to the resistance in the gas or liquid film around the catalyst particles was confirmed by the observation that changes in catalyst bed length for identical values of space time did not lead to different conversion levels.

Kinetic data. First, a series of experiments was conducted to establish the kinetic rate equation for the conversion of synthesis gas over catalysts of this type. In these experiments, a catalyst with a particle size of 0.38 mm and an average pore diameter of 150 nm was used (catalyst 5). Synthesis gas was converted at a temperature of 493 K, a pressure of 2.1 MPa, and at various space velocities and H_2/CO feed ratios.

It was found that, for this type of cobalt FT catalyst under the reaction conditions studied, the synthesis of hydrocarbons proceeds almost exclusively via the reaction:

$$n\mathrm{CO} + m\mathrm{H}_2 \rightarrow C_n\mathrm{H}_{2(m-n)} + n\mathrm{H}_2\mathrm{O},$$

and that the conversion of carbon monoxide and the production of hydrogen by the water-gas shift reaction can be neglected. The rates of conversion of carbon monoxide ($-r_{CO}$) and hydrogen ($-r_H$) have been expressed in terms of concentrations of hydrogen (C_H) and carbon monoxide (C_{CO}) in the gas phase via the equation:

$$-r_{CO} = -\frac{1}{UR} r_H = k_{CO} C_H^a C_{CO}^b \tag{1}$$

where UR is the H_2/CO usage ratio, m/n, and k_{CO} denotes the rate constant for CO conversion. On the basis of literature data on iron catalysts (see, for example: Dry et al., 1972; Feimer et al., 1981; Huff and Satterfield, 1984; Karn et al., 1965; Satterfield and Huff, 1980; Vannice, 1976) it was checked whether our experimental results on the cobalt catalyst could be described by a rate equation that was first order in hydrogen gas-phase concentration (i.e., $a = 1$) and zero order in carbon monoxide gas-phase concentration ($b = 0$). In that case, for a plug-flow reactor, the relation between space time, τ_s, the conversion of CO (χ_{CO}), hydrogen pressure in the reactor (p_H) and CO pressure at the reactor inlet (p_{CO}^0) can be written as (Levenspiel, 1972):

$$\tau_s = p_{CO}^0 \int_0^{\chi_{CO}} \frac{d\chi_{CO}}{k_{CO} p_H} \tag{2}$$

Taking into account the gas contraction, ϵ_g, which occurs during the conversion, Eq. 2 can be transformed into:

$$k_{CO}\tau_s = \int_0^{\chi_{CO}} \frac{(1 + \epsilon_g \chi_{CO})}{\mathrm{FR}\left(1 - \frac{\mathrm{UR}}{\mathrm{FR}}\chi_{CO}\right)} d\chi_{CO} \tag{3}$$

where $\mathrm{FR} = p_H^0/p_{CO}^0$.

Integration of Eq. 3 gives:

$$k_{CO}\tau_s = \frac{\epsilon_g}{(\mathrm{UR})^2}\ln\left(1 - \frac{\mathrm{UR}}{\mathrm{FR}}\chi_{CO}\right) - \frac{\epsilon_g}{\mathrm{UR}}\chi_{CO}$$

$$\tau_s = \frac{3{,}600}{\mathrm{GHSV}} \times \frac{273}{T} \times \frac{p^0}{10^5}, \tag{4}$$

where p^0 denotes the total pressure of hydrogen and carbon monoxide at the reactor inlet. The gas contraction, ϵ_g, can be conveniently expressed as a function of the H_2/CO feed and usage ratios:

$$\epsilon_g = -\frac{UR}{FR + 1} \quad (UR \leq FR)$$

or

$$\epsilon_g = -\frac{FR}{FR + 1} \quad (UR \geq FR)$$

when it is assumed that the volume of gaseous hydrocarbons formed can be neglected with respect to that of unconverted synthesis gas and water vapor formed.

The results given in Table 3 and Figure 1, obtained with crushed catalyst particles (catalyst 5), show that the first-order rate constant for carbon monoxide conversion, k_{CO}, calculated on the basis of Eq. 4, is fairly independent of space velocity and H_2/CO feed ratio. This demonstrates the validity of the kinetic expression.

Effect of particle size and pore diameter. The study of possible intraparticle diffusion effects was invariably carried out with synthesis gas having a H_2/CO feed ratio of 2 mol/mol. As the H_2/CO usage ratios observed were also very close to 2 mol/mol in this case, the gas contraction, ϵ_g, has a value of $-2/3$, and Eq. 4 can be simplified to:

$$k_{CO}\tau_s = -\frac{1}{6}\ln(1 - \chi_{CO}) + \frac{1}{3}\chi_{CO} \tag{5}$$

In order to allow a proper comparison of chemical conversion rates with transport (diffusional) rates of the reactants, it is more convenient to express Eq. 5 in terms of hydrogen conversion and the rate constant for hydrogen conversion, k_H, since rates of conversion depend on hydrogen pressure rather than on carbon monoxide pressure. The relation between k_H and k_{CO} follows for stoichiometry considerations:

$$-r_{CO} = k_{CO}C_H = -\frac{1}{2}r_H = \frac{1}{2}k_H C_H \tag{6}$$

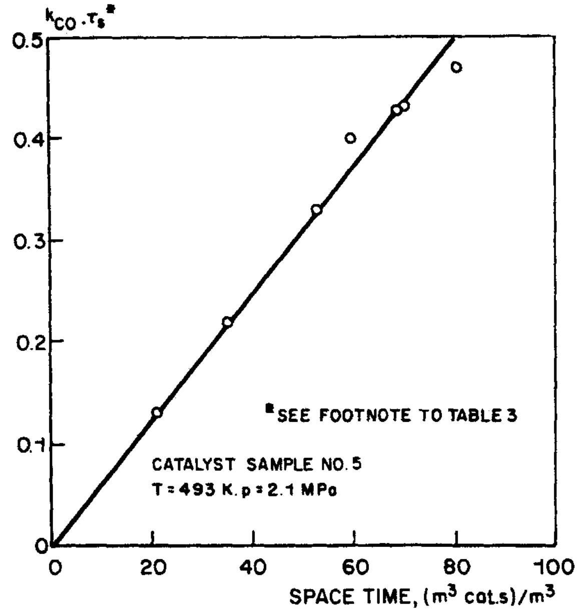


Figure 1. Test of first-order kinetics for plug-flow reactor.

and the integrated rate equation in terms of k_H can then be expressed as:

$$k_H\tau_s = -\frac{1}{3}\ln(1 - \chi_H) + \frac{2}{3}\chi_H \tag{7}$$

Table 4 summarizes the results obtained with catalysts 6, 7, and 8, in the conversion of stoichiometric synthesis gas ($H_2/CO = 2$ mol/mol) at a pressure of 2.1 MPa, at temperatures in the range 473–513 K, and at various space velocities. The rate constants for hydrogen conversion were calculated via Eq. 7.

Figure 2a shows the results obtained with a series of "wide-pore" (50–65 nm pore dia.) cobalt catalysts of similar chemical compositions and porous textures. Catalyst activity, expressed as observed first-order rate constant for hydrogen conversion, decreases significantly with increasing particle size and this is observed over the entire range of temperatures studied. The apparent activation energy for hydrogen conversion observed with the catalyst supported on 2.4 mm silica spheres is of the

Table 3. Effect of Space Velocity and Composition of Synthesis Gas Feed on CO Conversion*

Condition	Number						
	1	2	3	4	5	6	7
GHSV, $[Nm^3(H_2 + CO)]/(m^3 \text{cat} \cdot h)$	520	610	700	790	600	1,200	2,000
FR = H_2/CO feed ratio, mol/mol	1.9	2.4	2.9	3.4	2.0	2.0	2.0
UR = H_2/CO usage ratio, mol/mol	2.0	2.1	2.2	2.2	2.0	2.0	2.0
Conversion of CO, % mol	72	83	96	99	70	41	25
$k_{CO}\cdot\tau_s$**	0.47	0.43	0.40	0.33	0.43	0.22	0.13
τ_s, $(m^3 \text{cat} \cdot s)/m^3$	80.5	68.7	59.8	53.0	69.8	34.9	20.9
k_{CO}, $10^{-4}\ m^3/(m^3 \text{cat} \cdot s)$	58	62	67	62	62	64	62

*Over a zirconium-promoted cobalt Fischer-Tropsch catalyst: feed = H_2 + CO; reaction temperature = 493 K; pressure = 2.1 MPa; catalyst = No. 5
**Calculated from right-hand part of Eq. 4.

Table 4. Effect of Particle Size of Zr-Promoted Cobalt Fischer-Tropsch Catalyst on H_2 Conversion*

Catalyst		Reaction Conditions		Catalyst Performance				
Sample No.	Part. Dia. (2*R*) mm	*T* K	GHSV $Nm^3(H_2 + CO)/(m^3\ cat \cdot h)$	Conv. of H_2 % mol	*k*** $10^{-4}\ m^3/(m^3\ cat \cdot s)$	k^0† $10^{-4}\ m^3/(m^3\ cat \cdot s)$	$\eta = k/k^0$	$\phi = (R^2k^0/D)^{1/2}$††
6C	0.38	493	2,000	27	136	136	1.0	0.65
		498	2,000	34	178	178	1.0	0.73
		508	2,000	55	314	314	1.0	0.97
		513	2,000	65	392	410	0.96	1.1
6B	1.4	493	600	65	112	136	0.81	2.4
		503	900	61	158	260	0.61	3.3
		513	1,200	65	236	410	0.58	4.1
6A	2.4	496	2,000	18	90	154	0.58	4.3
		509	2,000	26	134	340	0.39	6.4
		513	1,000	52	146	410	0.37	7.0
7C	0.38	473.5	600	36	54	54	1.0	0.40
		483	900	40	92	100	~1.0	0.55
		493	1,500	49	200	192	~1.0	0.76
		503	1,200	85	352	360	~1.0	1.0
7B	0.75	483	600	58	92	100	~1.0	1.1
		492.5	900	63	164	184	0.89	1.5
		503	900	90	300	360	0.83	2.1
7A	2.4	474	600	27	40	54	0.74	2.5
		483	600	41	64	100	0.64	3.5
		493	840	42	94	192	0.49	4.8
		503	600	80	158	360	0.44	6.6
		513	840	79	220	680	0.32	9.0
8B	0.38	480	2,000	15	74	74	1.0	0.47
		490	2,000	27	136	134	1.0	0.64
		499	2,000	42	224	224	1.0	0.82
		503	2,000	49	268	280	~1.0	0.92
		513	2,000	78	510	500	~1.0	1.2
8A	2.6	490	2,000	16	76	134	0.57	4.3
		502	2,000	24	122	270	0.45	6.2
		511	2,000	30	158	480	0.33	8.2
		511	1,000	56	160			
		511	600	78	154			

*Feed = $H_2 + CO$; H_2/CO = 2 mol/mol; pressure = 2.1 MPa

**Actual (observed) rate constant for hydrogen conversion

†Intrinsic rate constant (without diffusion limitations)

††*D* = apparent effective diffusivity of hydrogen, taken as $1.2 \times 10^{-9}\ m^2/s$

order of 60–70 kJ/mol and is about half of that found for the catalyst sample having a particle size in the submillimeter range (120 kJ/mol). A similar effect of particle size and temperature on rate constant is found for a series of "narrow-pore" (10–15 nm pore dia.) cobalt catalysts, as is illustrated in Figure 2b. Both the substantial loss in activity observed with larger catalyst particles and much lower energy of activation, indicate that intraparticle mass-transfer limitations play a significant role in catalysts with particle sizes in excess of about 1 mm. It has been verified in separate experiments using, for example, temperature-programmed reduction, that variation of the particle size within a series of cobalt catalysts of similar chemical composition and porous texture has no effect on the response of the catalyst to the reductive pretreatment applied. This means that the observed differences in performance are due entirely to physical effects (i.e., diffusion limitations), as chemical effects such as differences in degree or state of reduction can be ruled out.

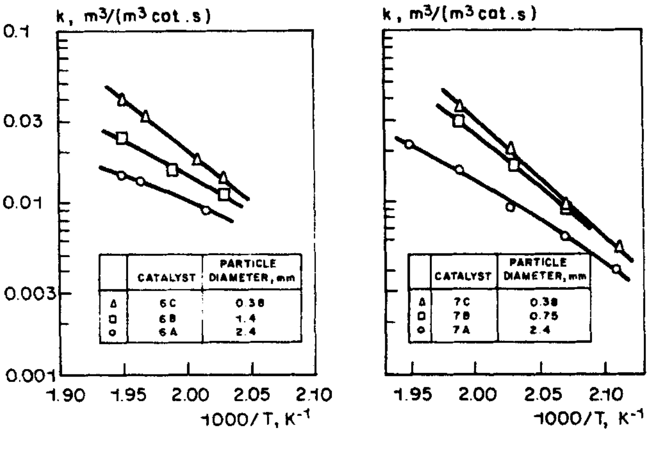
The effect of particle size on reaction rate can be quantified using the well-known relation between effectiveness factor, η (defined as the ratio between observed rate constant, k, and the intrinsic rate constant, k^0) and the Thiele modulus, ϕ. For spherical particles (radius, R) and first-order kinetics, the relation can be expressed as

$$\eta = \frac{3}{\phi}\left(\frac{1}{\tanh \phi} - \frac{1}{\phi}\right) \tag{8}$$

where

$$\phi = \left(\frac{R^2k^0}{D}\right)^{1/2}$$

The intrinsic first-order rate constant for hydrogen conversion was taken as the rate constant observed with crushed catalyst material having an average particle size of 0.38 mm. The diffusion constant, D, appearing in the Thiele modulus, should be considered as an apparent effective diffusivity of hydrogen,



A. WIDE-PORE CATALYSTS

B. NARROW-PORE CATALYSTS

Figure 2. Effect of catalyst particle size on Fischer-Tropsch synthesis of hydrocarbons.
First-order rate constants for hydrogen conversion over zirconium-promoted cobalt-on-silica catalysts

based on gas-phase concentrations, to be used in combination with the current kinetic expression. The value of D was determined graphically, as shown in Figure 3, where we have recalculated the relationship between η and ϕ in terms of a relation between η and D, with different values of R^2k^0 as parametric curves. The experimental results, i.e., combinations of η and R^2k^0, yield a set of diffusivities of very satisfactory consistency. An average value for D, of 1.2×10^{-9} m²/s, is obtained and proved to be independent of the pore diameter, which was varied in the range, 10–65 nm. The consistency of the results is also apparent from Figure 4, which shows a fit of the experimental data to the Thiele relation.

Discussion

The involvement of diffusion limitations in FT catalyst particles with dimensions in the millimeter range, is demonstrated in the previous section and is particularly supported by the effect of particle size on energy of activation and by the almost perfect fit of the experimental results to the Thiele relation. The question that now needs to be addressed concerns the physical significance of the apparent effective hydrogen diffusivity, D, emerging from the Thiele relation. Though D is based (owing to the kinetic expression used) on gas-phase concentrations, the idea that the transport-limiting step originates from diffusion of hydrogen in gas-filled pores can be ruled out. Gas-phase diffusion proceeds orders of magnitude faster than a transport process characterized by a diffusivity of about 10^{-9} m²/s. Moreover, the class of cobalt catalysts under discussion shows a high tendency to form high-molecular-weight hydrocarbons, as illustrated by the Anderson-Flory-Schulz plot, shown in Figure 5,

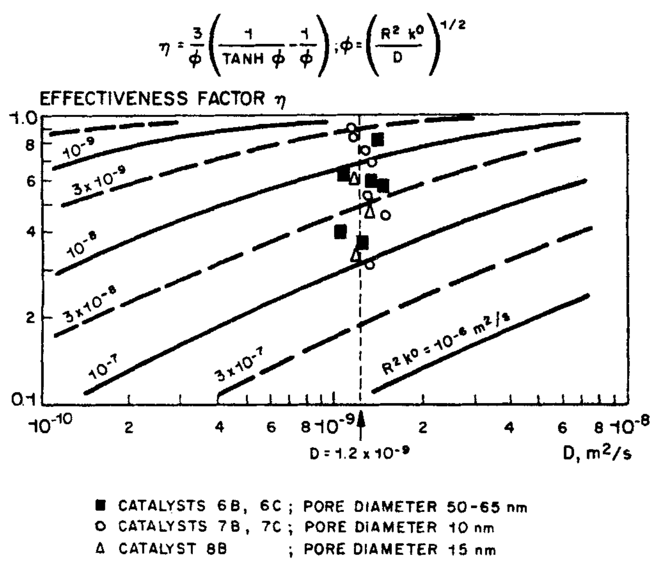


Figure 3. Graphical determination of diffusivity from Thiele relation.

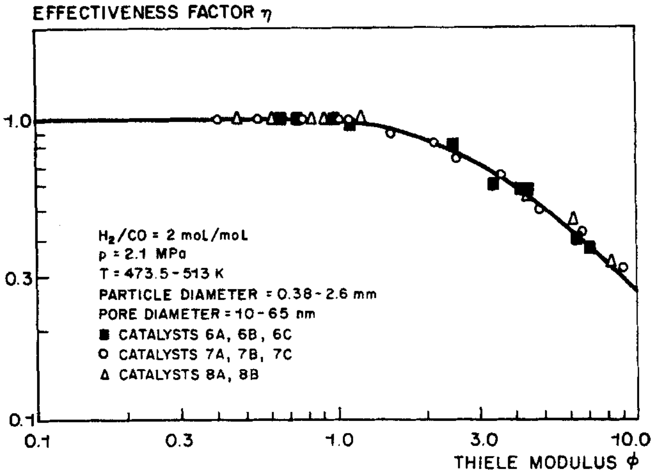


Figure 4. Fit of Table 4 data to the Thiele relation.
$D = 1.2 \times 10^{-9}$ m²/s

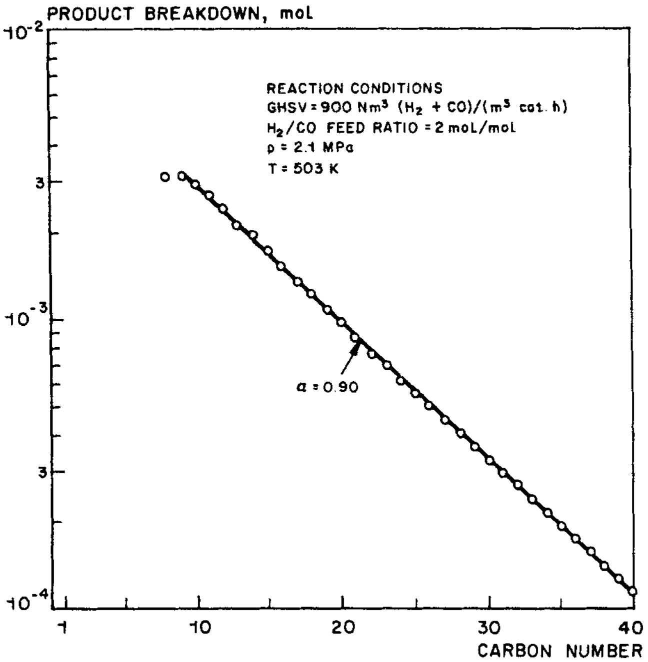


Figure 5. Carbon number distribution of C_{8+} product.
Obtained with zirconium-promoted cobalt-on-silica catalyst, No. 5, Table 1.

Table 5. Estimate of H_2 Diffusivity in a Heavy Paraffinic Fischer-Tropsch Product

$D_m = 7.4 \times 10^{-12}\, T(XM)^{0.5}/\mu V_o^{0.6}$ (Wilke and Chang, 1955)
D_m = molecular diffusivity of solute, m^2/s, based on liquid-phase conc.
μ = solution viscosity, centipoise (10^{-3} N · s/m^2)
T = absolute temperature, K
X = association parameter
M = solvent molecular weight, kg/kmol
V_o = molar volume of solute at normal boiling point, 10^{-6} m^3/mol

$\mu = 0.6$ cp $= 0.6 \times 10^{-3}$ N · s/m^2
$T = 500$ K
$X = 1$
$M = 300$ kg/kmol
$(V_o)_{H_2} = 14.3 \times 10^{-6}$ m^3/mol

Hence:
$D_m(H_2) \simeq 2.2 \times 10^{-8}$ m^2/s (based on liquid-phase conc.)

from which a high growth chance can be deduced, typically of the order of 0.9. Under reaction conditions the major part of the hydrocarbon product will be in the liquid phase. The liquid will fill the pores of the catalyst carrier material so that transport of hydrogen and carbon monoxide to the reactive sites occurs by diffusion of these reactants through this liquid medium inside the pores.

The apparent effective diffusivity, D, can be related to the molecular diffusivity, $D_m(H_2)$ and solubility, $H(H_2)$ of hydrogen in the paraffinic liquid by the following expression:

$$D = D_m(H_2)\frac{\epsilon}{\tau}RT \cdot H(H_2). \qquad (9)$$

The catalyst particle porosity, ϵ (based on total catalyst bed volume) has a value of about 0.40 for the catalyst samples investigated. The tortuosity, τ, is expected to have a value in the range, 1.0–2.0. The solubility of hydrogen in a heavy paraffinic liquid (average molecular weight, 300–400 kg/kmol; density, 650 kg/m^3; temperature, 500 K) was obtained by interpolation of data from Kölbel et al. (1955) and Peter and Weinert (1955) and is estimated to be of the order of 5×10^{-5} mol/(m^3 · Pa). Using the correlation proposed by Wilke and Chang (1955) to predict the molecular diffusivity of hydrogen in the liquid phase in the catalyst pores (cf., Table 5), we thus arrive at a value for D in the range, 0.9×10^{-9} m^2/s–1.8×10^{-9} m^2/s, which is in excellent agreement with the experimental value obtained from the Thiele relation. Apparently, the limited bulk diffusion of hydrogen through the heavy paraffinic product present in the catalyst pores at reaction conditions is the origin of retardation of reaction rates in larger catalyst particles, and this conclusion is fully compatible with the observation that the extent of diffusion limitation is independent of pore diameter.

Conclusions

Reaction rates in Fischer-Tropsch synthesis with iron and cobalt catalysts are seriously limited by intraparticle diffusion of hydrogen for catalyst particle diameters in excess of about 1 mm. This intraparticle diffusion is, in essence, diffusion through pores filled with liquid Fischer-Tropsch product. The experimentally determined reaction rates were in excellent agreement with the Thiele model, using diffusivities estimated according to well-known correlations for liquid diffusivities, corrected for porosity and tortuosity.

Acknowledgment

The authors gratefully acknowledge the contribution of H.J.M. Bijwaard to the present study.

Notation

C_A = concentration of reactant, A, in gas phase, mol/m^3
D = apparent effective hydrogen diffusivity, based on gas-phase conc., m^2/s
$D_m(H_2)$ = molecular diffusivity of hydrogen, based on liquid-phase conc., m^2/s
FR = H_2/CO feed ratio, mol/mol
GHSV = gas hourly space velocity of synthesis gas, Nm^3(H_2 + CO)/(m^3 cat · h)
$H(H_2)$ = solubility (Henry's constant) of hydrogen in liquid paraffinic FT product, mol/(m^3 · Pa)
k_{CO} = first-order rate constant for CO conversion, m^3/(m^3 cat · s)
$k = k_H$ = first-order rate constant for hydrogen conversion, m^3/(m^3 cat · s)
k^0 = intrinsic first-order rate constant for hydrogen conversion (without diffusion limitations), m^3/(m^3 cat · s)
p^0 = pressure of synthesis gas at reactor inlet, Pa
P_A = pressure of reactant, A, in reactor, Pa
P_A^0 = pressure of reactant, A, at reactor inlet, Pa
R = particle radius, m
R, Eq. 9 = gas constant, 8.3144 (m^3 · Pa)/(K · mol)
$-r_A$ = rate of conversion of reactant, A, per unit catalyst bed volume, mol/(m^3 cat · s)
T = temperature, K
UR = H_2/CO usage ratio, mol/mol

Greek letters

α = Anderson-Flory-Schulz growth chance
ϵ = porosity, $\dfrac{\text{catalyst pore volume}}{\text{volume of catalyst bed}}$
ϵ_g = gas contraction
η = effectiveness factor
τ = tortuosity
τ_s = space time, (m^3*cat* · s)/m^3
ϕ = Thiele modulus
χ_A = conversion of reactant, A

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