ELSEVIER

Chemical Engineering Journal 82 (2001) 13–20

Chemical Engineering Journal

www.elsevier.com/locate/cej

Eggshell catalysts for Fischer–Tropsch synthesis Modeling catalyst impregnation

C. Galarraga [a], E. Peluso [a], H. de Lasa [b],*

[a] PDVSA-INTEVEP, Apdo 76343, Caracas 1070, Venezuela

[b] CREC, Faculty of Engineering, University of Western Ontario, London, Ont., Canada N6A 5B9

Received 15 May 2000; accepted 13 October 2000

Abstract

This study presents a successful methodology to produce Co–Zr on silica eggshell catalysts. It is shown that parameters such as impregnation time, metal solution concentration, solution viscosity, as well as the state of the support before impregnation, strongly influence the evolution of the thickness and the final state of the metal in the eggshell catalyst. It is demonstrated that the wet impregnation, using low metal concentration solutions improves metal dispersion by producing a more progressive eggshell profile than the dry impregnation.

Mathematical models were used to describe both the dry impregnation, effected with low and high metal concentration solutions, as well as the wet impregnation, effected with low metal concentration solutions. These models include either no adjustable parameter (dry impregnation) or a single adjustable parameter (wet impregnation) and lead to reliable predictions of the formation of the eggshell.

Keywords: Eggshell catalyst; Fischer–Tropsch synthesis; Impregnation

1. Introduction

The synthesis of middle distillate hydrocarbons via Fischer–Tropsch synthesis (FTS) is a process strongly influenced by intra-catalyst mass transport limitations. These mass transport limitations are due to the relatively slow diffusion of high-molecular weight paraffins inside the catalyst pores. To address these problems eggshell catalysts have been proposed [1].

Eggshell catalysts can be engineered with an active phase deposited in the outer region of the catalyst pellet [2]. Minhas and Carberry [3], Horvath and Engasser [4] found that the so-called eggshell catalysts were superior to the uniform impregnated ones for enzymatic and for oxidation reactions. Lee and Aris [5] outlined, from a modeling perspective, the conditions leading to the superior performance of eggshell catalysts. Komiyama [6], Maatman and Prater [7], and Gavriilidis et al. [8], attempted to control the impregnation profiles for more effective and selective catalysts. In this respect a valuable review of the topic was published by Yeung et al. [9].

Regarding Fischer–Tropsch synthesis, Zimmerman et al. [10] reported that catalytic activity was controlled in wax-filled pores of fused iron catalysts, by the low diffusivity of the reactants. In this respect, smaller than 0.2 mm pellets were suggested to avoid mass transport restrictions. However, eggshell catalyst close to 2 mm particle diameter can allow to overcome diffusional problems in fixed bed reactors, with these reactors having acceptable pressure drops and flow patterns [11].

Preparation conditions can affect the metal distribution of the so-called “eggshell” or “pellicular” catalysts [1,2,5,12,13]. Relevant preparation parameters include metal concentration in solution, solution viscosity, support condition (dry or wet) and impregnation time. These parameters can affect the eggshell thickness evolution (metal distribution), the metal morphology and the metal crystallite size [14]. Thus, better understanding of various preparation parameters can allow taking full advantage of the eggshell catalysts reducing intra-particle mass transport and achieving high yields of desired middle distillate paraffinic hydrocarbons.

Peluso et al. [14] and Galarraga et al. [15] demonstrated that preparation conditions of a Co–Zr on silica eggshell catalyst influence the production of middle distillates and particularly the C_{10}–C_{20} hydrocarbon fraction. On this basis, it is established that an optimum eggshell catalyst should have

---

* Corresponding author. Tel.: +1-519-661-2144; fax: +1-519-661-3498. *E-mail addresses:* hdelasa@eng.crec.uwo, hdelasa@julian.uwo.ca (H. de Lasa).

1385-8947/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S1385-8947(00)00352-1

Nomenclature

C	concentration of metal at "r" inside the spherical pellet (kg Co/m^3)
C_o	concentration of cobalt on the outer surface of the spherical pellet (kg Co/m^3)
D_{eff}	effective diffusivity (cm^2/s)
K_d	permeability coefficient (cm^2/s)
n	number of terms used in the series (Eq. (19))
N_{air}	moles of air (moles)
P	pressure (kPa)
P_a	atmospheric pressure (kPa)
P_c	capillary pressure (kPa)
P_o	saturation pressure (kPa)
P_r	pressure with liquid front at r radial position (kPa)
P_{R_o}	pressure with liquid front at radial position R_o (kPa)
Q	impregnating solution volumetric flow (cm^3/s)
r	radial coordinate in the spherical pellet (cm)
r_c	capillary radius (cm)
r_p	pore radius (cm)
R	universal gas constant (kPa cm^3/mol K)
R_o	pellet radius (cm)
t	impregnation time (s)
T	temperature (°C)
v	impregnation liquid velocity (cm/s)
V_r	volume of the sphere of "r" radius (cm^3)

Subscripts

r	radial coordinate (m)
$r=0$	center of the pellet
R_o	outer radius of the pellet (m)

Greek symbols

ε	porosity
γ	surface tension (dyn/cm)
μ	viscosity of the impregnating solution (cP)
θ	contact angle between the impregnating solution and the support (°).
ρ	density of the impregnating solution (kg/m^3)
σ	$2\gamma\cos\theta/(r_c P_a)$

Table 1
Comparison of the performance of one of the eggshell catalyst of this study with the uniformly impregnated catalyst[a,b]

Catalyst	Rate of CO consumption (mmol/min g of Co)	"α" parameter Anderson–Shultz–Flory distribution (ASF)
Eggshell	−0.01435	0.8
Uniformly impregnated	−0.00813	0.9

[a] $T = 220°\mathrm{C}$, $P = 1.52\,\mathrm{MPa}$, GHSV $= 324\,\mathrm{h}^{-1}$, $H_2/CO = 2$.

[b] Eggshell catalyst prepared as follows: (a) impregnation time:4 s, (b) viscosity of the impregnating solution: 2 cP, (c) concentration of cobalt in the impregnating solution: 0.1 g of Co/ml, (d) method: wet impregnation.

10 wt.% Co deposited in about the half radius of a 1.81 mm diameter particle. This eggshell catalyst displays while compared with the performance of the uniformly impregnated catalyst (Table 1) encouraging CO conversion selectivity, yielding 65 wt.% hydrocarbons in the diesel range [14,15].

Thus, given the significance of eggshell catalysts for Fischer–Tropsch synthesis, it is the goal of the present study to develop mathematical models for the formation of the eggshell catalysts. It is also the objective of the present contribution to develop models that could be used in the context of dry metal impregnation and of wet metal impregnation. In addition, it is desirable that these models should include a minimum number of adjustable parameters making the modeling of the eggshell formation process very reliable.

2. Modeling the impregnation with dry solids

Modeling the egg catalyst impregnation in a porous dry particle, can be developed adopting the following assumptions [5]: (a) a front of liquid is moving inside a spherical pellet, (b) the Darcy's law can be applied to describe motion of Newtonian fluids, (c) the permeability coefficient is constant, (d) the gravity force is negligible while compared to the viscous and the capillary forces, (e) capillary forces can be modeled using a representative pore size, (f) properties of the impregnating liquid remain constant during the impregnation process.

Thus, for a spherical particle, having a R_o radius, and being impregnated under atmospheric pressure, the Darcy's law flow describes the velocity of the liquid front across the particle as a function of the permeability coefficient, K_d, the solution viscosity, μ, and the pressure in the system:

$$v(r) = \frac{K_d}{\mu}\frac{dP}{dr} \tag{1}$$

As well the volumetric impregnation solution flow across the particle can be expressed as:

$$Q(t) = v(r) 4\pi r^2 \varepsilon \tag{2}$$

or

$$v(r) = \frac{Q(t)}{4\pi\varepsilon r^2} \tag{3}$$

Thus, considering Eqs. (1)–(3) it follows that:

$$\frac{Q(t)}{4\pi\varepsilon r^2} = \frac{K_d}{\mu}\frac{dP}{dr} \tag{4}$$

which can be rearranged to obtain

$$\int_{P_r}^{P_{R_o}} dP = \frac{Q(t)\mu}{K_d 4\pi\varepsilon}\int_r^R \frac{dr}{r^2} \tag{5}$$

Integrating Eq. (5) between the outer radius, R_o, and the radius, r, and rearranging it results:

$$P_r = P_{R_o} - \frac{\mu}{K_d}\frac{Q(t)}{4\pi\varepsilon}\left[\frac{1}{r} - \frac{1}{R_o}\right] \tag{6}$$

In addition to this for a dry particle with liquid being forced from the outer surface, the number of air moles trapped inside the particle remains constant. Thus, at the initial condition and before the liquid start evolving in the particle it results:

$$N_{air} = \frac{P_a V_{R_o}}{RT} \tag{7}$$

with

$$V_{R_o} = \tfrac{4}{3}\pi R_o^3 \varepsilon \tag{8}$$

However, when the liquid front reach the distance, r, and given conservation it follows:

$$N_{air} = \frac{(P_r + P_c)V_r}{RT} \tag{9}$$

where

$$V_r = \tfrac{4}{3}\pi r^3 \varepsilon \tag{10}$$

Combining Eqs. (7)–(10), it results

$$P_r = P_{R_o}\frac{R_o^3}{r^3} - P_c \tag{11}$$

The capillary pressure involved in Eq. (11), is a function of the surface tension, γ, the wetting contact angle, θ, and the capillary radius (or pore radius), r_c, and it can be described according to:

$$P_c = \frac{2\gamma\cos\theta}{r_c} \tag{12}$$

Therefore, Eq. (11) can be expressed as

$$P_r = P_{R_o}\frac{R_o^3}{r^3} - \frac{2\gamma\cos\theta}{r_c} \tag{13}$$

Equating Eqs. (6) and (13), it follows that:

$$P_{R_o}\frac{R_o^3}{r^3} - \frac{2\gamma\cos\theta}{r_c} = P_{R_o} - \frac{\mu}{K_d}\frac{Q(t)}{4\pi\varepsilon}\left[\frac{1}{r} - \frac{1}{R_o}\right] \tag{14}$$

Rearranging the resulting equation it results:

$$P_{R_o}\left(\frac{R_o^3}{r^3} - 1\right) = \frac{2\gamma\cos\theta}{r_c} - \frac{\mu}{K_d}\frac{Q(t)}{4\pi\varepsilon}\left[\frac{1}{r} - \frac{1}{R_o}\right] \tag{15}$$

where $Q(t)$ can be expressed as follows:

$$Q(t) = \frac{\mathrm{d}((4/3)\pi R_o^3 - (4/3)\pi r^3)\varepsilon}{\mathrm{d}t} = 4\pi\varepsilon r^2\frac{\mathrm{d}r}{\mathrm{d}t} \tag{16}$$

Thus, substituting $Q(t)$ into Eq. (15), it results:

$$\frac{\mathrm{d}(1 - (1/R_o))}{\mathrm{d}t} = \frac{K_d P_a}{\mu R_o^2}\frac{[1 + \sigma - (R_o/r)^3]}{((R_o/r) - 1)}\left(\frac{R_o}{r}\right)^2 \tag{17}$$

where $\sigma = (2\gamma\cos\theta / r_c P_a)$ is a dimensionless capillary pressure, r_c the pore radius (r_p) and P_{R_o} the atmospheric pressure (P_a).

While there is a proposed analytical solution for Eq. (17) [5] a numerical solution of this ordinary differential equation is preferred, in the present study, given this allows to describe impregnation phenomena with parameters changing eventually with impregnation time.

3. Modeling of the impregnation process in wet solids

An alternative impregnation model can be considered for the case of a spherical porous solid wet prior to impregnation. In this case, the process of impregnation mainly proceeds via diffusion with resulting metal concentration being a function of time and radial position. The following equation can, then, be considered [16]:

$$\frac{\partial C}{\partial t} = D_{eff}\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \tag{18}$$

For the wet catalyst impregnation of the present study, the following assumptions can be adopted: (a) the initial concentration of the impregnating solution, C_o, inside the particle is zero, (b) the initial concentration of the impregnating solution, C_o, at the particle outer surface is constant, (c) the diffusive flow is a function of an effective diffusivity parameter, D_{eff}.

Thus, the change in impregnating solution concentration in a solid sphere can be expressed as

$$\frac{C}{C_o} = 1 + \frac{2R_o}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi r}{R_o}\right)\mathrm{e}^{-(D_{eff}n^2\pi^2 t/R_o^2)} \tag{19}$$

Moreover, calculations of the impregnating solution concentration at the center of the particle has to be calculated with the following alternative equation:

$$\frac{C_{r=0}}{C_o} = 1 + 2\sum_{n=1}^{\infty}(-1)^n\,\mathrm{e}^{-(D_{eff}n^2\pi^2 t/R_o^2)} \tag{20}$$

The solution of Eqs. (19) and (20) requires the estimation of an effective diffusivity. This parameter will be defined, as it will be shown in the upcoming section of this manuscript, as the result of a numerical regression process.

4. Experimental procedure and parameter estimation

To prepare the eggshell catalysts a silica support (DAR-240 from UOP) with a 372 $\mathrm{m^2/g}$ specific surface area and a 1.81 mm average particle diameter was selected [12].

Eggshell catalysts were prepared by carefully controlling the impregnation time. The following methodological steps were adopted: (a) the desired amount of support was placed into a fritted glass funnel mounted on a flask connected to

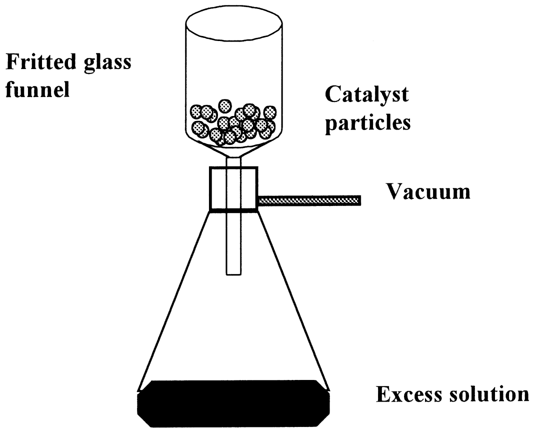

Fig. 1. Experimental set-up used for the preparation of the eggshell catalysts.

a vacuum system; (b) the impregnating solution was poured onto the support in a volume ratio solution/support of about 5, (c) after the desired impregnation time was reached (between 5 and 60 s) the excess solution was rapidly evacuated from to the flask by connecting the vacuum to the system. A schematic representation of the equipment used for the support impregnation is reported in Fig. 1.

While for dry impregnation, the support was directly used as received from the silica manufacturer, for the case of wet impregnation the support was pre-wetted with water. No excess of water was allowed on top of the particles (or in between particles). In addition and to change the viscosity of the solution from 2 to 40 cP (0.1 g Co/ml solution), hydroxyethyl-cellulose (in a concentration of 1 wt.%) was added in the water solution as viscosifying agent [2].

The impregnating solution was constituted by a cobalt nitrate solution with close to 5 wt.% zirconia promoter content (based on the combined Zr + Co metal content). Once the support impregnated it was transferred to a fluidized bed made out of sand particles (60 μm average size), and kept at 90°C. The goal of this operation was to “freeze”, at this temperature, the movement of the solution inside the pores of the support. This was achieved given the excellent heat transfer conditions in the fluidized bed enhancing fast drying. As well, the drying under fluidized conditions prevented the collapse of the catalyst porous structure given the close control of temperature in this unit.

Completed this step the impregnated catalyst samples were calcined at 400°C for about 5 h with the temperature being increased at the rate of 5°C/min. This methodology was adopted following preliminary studies showing that at these conditions there is complete decomposition of the cobalt precursor [17]. Also under these conditions little interactions between the cobalt and silica are expected and as a result it is believed that most of the impregnated cobalt should be available as active species for the hydrocarbon synthesis reaction [18]. The adequacy of this method was also confirmed using TPR and showing a high degree of reducibility of the cobalt species (72–98%) [15].

Five series of catalysts, forming 25 samples, were prepared in the present study. This was achieved changing various preparation conditions as reported in Table 2. In this respect, various impregnation times, viscosities of the impregnating solution, solution concentrations and state of the support before impregnation (dry or wet) were changed systematically. Dry and wet impregnation samples were analyzed using optical microscopy and SEM-EDX to determine metal concentration profiles.

In order to perform measurements of the “dimensionless penetration” or “eggshell thickness”, the catalysts were cast mounted in an epoxy resin. The molds were allowed to dry completely and they were polished until a smooth surface was achieved. Cross-sections of the catalyst pellets were observed by optical microscopy using a stereomicroscope Wild model M3Z, a 3CCD color Hitachi camera model HV-C20 and a color video printer Mavigraph from Sony, model UP-3000. Both camera and printer were fully assembled to the microscope so those pictures could be taken from different samples to determine the evolution of the eggshell.

In the case of the dry impregnation theoretical metal concentration profiles were calculated using the integrated form of Eq. (17). This allows calculating various dimensionless pellets positions reached by the impregnating solution at different impregnating times. There were no adjustable parameters with various model parameters determined independently. In the case of the wet impregnation the effective diffusivity was the only adjustable parameter and it was determined by optimizing the best fitting of experimental and theoretical results as given by Eqs. (19) and (20) securing a normal distribution of residuals with minimization of the following objective function, calculated as

$$\sum\left\{\left(\frac{C}{C_{\text{o}}}\right)_{\text{theoretical}}-\left(\frac{C}{C_{\text{o}}}\right)_{\text{experimental}}\right\}^2 \tag{21}$$

Table 2
Preparation conditions[a]

Series	Impregnation time (s)	Viscosity of the solution (cP)	Solution concentration (g cobalt/ml)	State of the support
A	4, 5, 6, 7, 8, 12, 16	2	0.10	Dry
B	4–5, 8, 12, 16, 25	2	0.10	Wet
C	4, 5, 12, 20, 40	5	0.20	Dry
D	4, 10, 20, 40	5	0.20	Wet
E	4, 20, 60	40	0.10	Dry

[a] Eggshell catalysts.

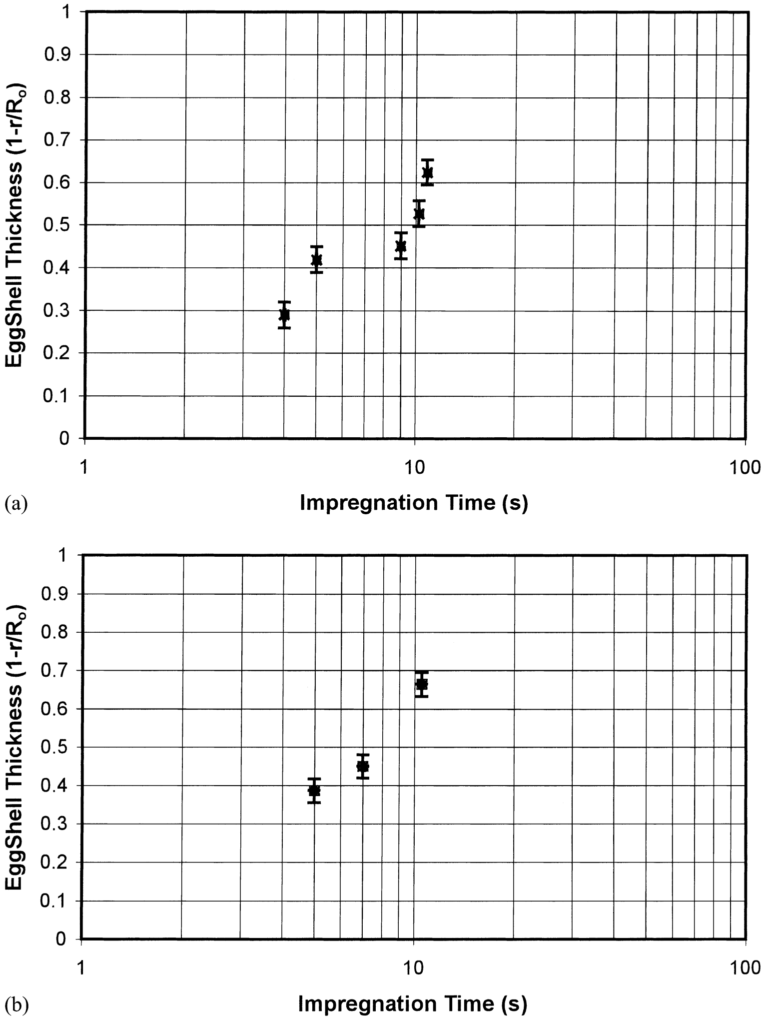

Fig. 2. (a) Measurements of the eggshell thickness in single particles of catalysts from the series B (viscosity $= 5\,\mathrm{cP}$ and dry support) using optical microscopy. (b) Measurements of average eggshell thickness for several particles of a same catalyst (series B) using optical microscopy.

5. Discussion of results

The experimental values of the dimensionless eggshell thickness were calculated using microphotographs of the catalyst cross-sections. Measurements were taken for each particle with random orientations. Note that in addition, the average eggshell thickness was defined using three to four particles.

Fig. 2 reports measurements taken of the eggshell thickness for single catalyst particles from the series B ($\mu = 5\,\mathrm{cP}$ and dry support) and averages values for several particles of the same series (series B). It can be noticed that data dispersion for single particles is in the 5% standard deviation while for a population of particles (4–5 particles) the standard deviation is close to 10%. It can be speculated that this increased standard deviation is due to the expected differences of the porous support network in between particles.

Regarding Eq. (17), it numerical solution provides the dimensionless penetration across the particle as a function of the impregnation time. Its application requires the definition of a number of characteristic parameters as reported in Table 3.

Eq. (17) is valuable to establish the asymptotic and expected behaviors during the impregnation process. It can be appreciated that when the impregnation process is about to be completed, $r \rightarrow R_o$ and consequently the group

Table 3
Parameters for simulation of impregnation profiles in dry supports

Parameter	Value	Reference
Surface tension (γ, dyn/cm)	67.5	[1]
Contact angle (θ, °)	0	[1]
Pore radius (r_p, cm)	5.51×10^{-7}	[12]
Viscosity (μ, cP)	2.02–5.18	[12]
Atmospheric pressure (P_a, kPa)	101	
Permeability (K_d, cm^2)	1.5×10^{-14}	[5]
Porosity (ε, dimensionless)	0.6401	[12]
Particle radius (R_o, cm)	0.0905	[12]

$((R_o/r)-1)\rightarrow 0$. Eq. (17) presents in this case, an indetermination yielding an infinite eggshell thickness. However, setting r close to R_o, Eq. (17) provides an important estimation of the minimum time required for complete support impregnation. This parameter is relevant for conditions where there is no air remaining entrapped inside the pores of the support. From a physical point of view, this condition is equivalent to assume that the air inside the pores have the opportunity of diffusing across the pellet and can escape towards the bulk of the impregnating solution.

Eq. (17) also predicts that the metal penetration in the pellet increases with impregnation time until a maximum value is reached. This maximum value is a characteristic parameter for a given system and it can be considered a function of σ [5]. This maximum penetration is a relevant parameter for the case when air remains entrapped in the particle core and the penetration arrests once a given eggshell thickness is reached. Under this condition, the velocity of the liquid front approaches zero ($v\rightarrow 0$) and equilibrium is attained with the head of the liquid balancing capillary forces and entrapped air pressure.

Regarding the experimental results of the present study the evolution of the dimensionless thickness with impregnation time on both dry and wet supports, as determined from optical microscopy, are reported in Fig. 3a and b. These figures report results for catalysts impregnated using low and high concentration of cobalt. For the catalysts here investigated it was found that the impregnation process of both series of catalysts (low and high concentration of cobalt in the solution) follows the expected trends closely. It can be observed that dry impregnation is a much faster process with impregnation being enhanced in low density and low viscosity solutions.

In order to investigate in more detail the applicable models for the evolution of dry impregnation the integrated form of Eq. (17) was compared to experimental data (Fig. 4). It can be observed that the dimensionless penetration, as predicted by the proposed model, follows the experiments developed and capture the two possible limiting impregnation behaviors: (a) eggshell formation with limited metal penetration, (b) eggshell formation without limited penetration and metal reaching the particle core.

In fact, for the low cobalt solution concentration (0.1 g of cobalt/ml or 0.499 g of $Co(NO_3)_2{\cdot}6H_2O$/ml) and a low viscosity, $\mu = 2$ cP (Fig. 5), the dimensionless penetration measured experimentally fitted well the model which neglected air entrapment. In this case, the dimensionless penetration parameter reaches, in the center of the particle, the value of one at about 10 s of penetration time. Therefore, the penetration process can proceed to completion and it can be argued that the air entrapped can escape from the pellet during impregnation. On the other hand, for higher cobalt concentrated solution (0.2 Co/ml or 0.998 g of $Co(NO_3)_2{\cdot}6H_2O$/ml) and a correspondingly higher viscosity (5 cP) the escape of the entrapped air appears to be severely hindered. Therefore there is, in this case, presumably a reduced total penetration and a maximum value for the dimensionless penetration thickness.

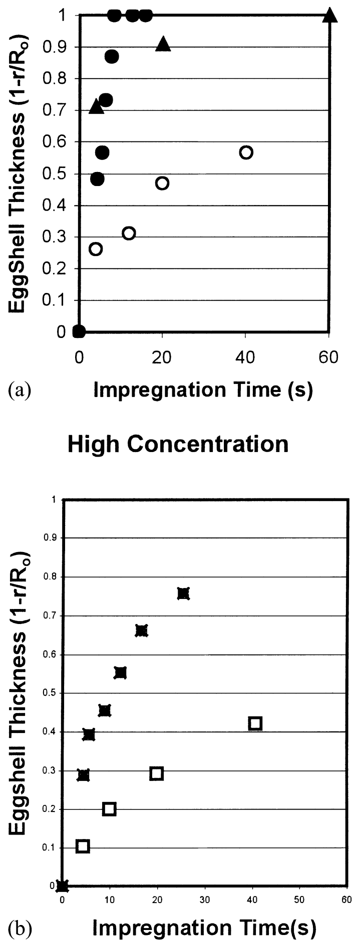

Fig. 3. Evolution of the eggshell thickness with impregnation time using optical microscopy. Includes catalyst prepared using dry and wet methods. (a) Low concentration: (●) 2cp-01-D; (▲) 40 cp-01-D; (○) 2cp-01-W. (b) High concentration (■) 5cp-02-D; (□) 5cp-02-W. Codes: (e.g. 2cp-01-D). The first three characters (2cp) refers to the viscosity of the solution in centipoises, the following two digits (01) refers to the concentration of the impregnating solution (0.1 of Co/ml), the last character refers to the state of the support (e.g. dry).

Regarding the metal concentration profiles using pre-wet samples, they were determined using SEM-EDX. Once this data available the following methodological steps were adopted: (a) numerical solution of the Eq. (19) for various diffusivities, (b) selection of the best fitting between the experimental and the theoretical data, and (c) determination of the effective diffusivity.

Comparison between experimental and simulated data is presented in Fig. 6. It is found that with a 1.3×10^{-5} cm^2/s ±8% effective diffusivity data is fitted adequately with normal distribution of residuals. This diffusivity falls within realistic values given that effective diffusivities for rhodium solutions impregnated on alumina were reported to be ranging from 0.3 to 1.0×10^{-5} cm^2/s [5,19].

It can also be mentioned that there is agreement in terms of effective diffusivities found for the sets of data obtained

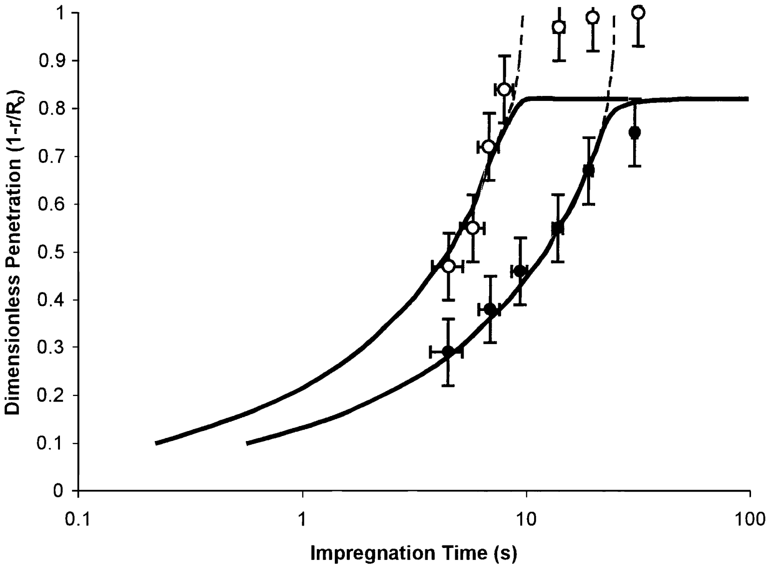

Fig. 4. Theoretical and experimental changes of dimensionless penetration parameter with time for high concentration (0.2 g Co/ml), and low cobalt concentration (0.1 g Co/ml) solutions. Broken lines: model excludes air entrapment. Solid lines: model includes entrapped air. Bars represents average error for a population of at least four particles. Experimental data corresponds to visual observations of the eggshell thickness using optical microscopy.

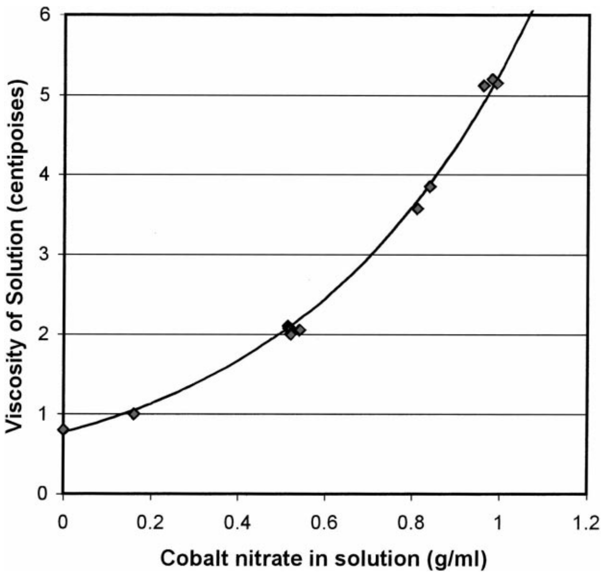

Fig. 5. Viscosity of the aqueous solutions of cobalt nitrate as a function of the concentration of cobalt nitrate in solution. 0.499 g $Co(NO_3)_2{\cdot}6H_2O$/ml is equivalent to 0.1 g of Co/ml.

Table 4
Effective diffusivities at various impregnation times[a]

Impregnation time (s)	Effective diffusivity, D_{eff} (cm/s)
4	$1.25 \times 10^{-5} \pm 8\%$
5	$1.30 \times 10^{-5} \pm 8\%$
12	$1.2 \times 10^{-5} \pm 8\%$

[a] Viscosity of the solution: 2 cP, concentration of the solution: 0.1 g Co/ml, state of the support before impregnation: wet. Reference code: 2cP-01-W.

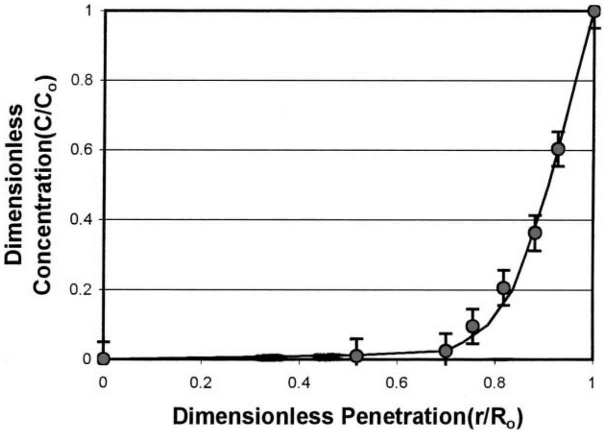

Fig. 6. Experimental and simulated data for wet impregnation using low concentrated solutions (0.1 g Co/ml or 0.499 g $Co(NO_3)_2{\cdot}6H_2O$/ml). Effective diffusivity was estimated to be $1.3 \times 10^{-5} \pm 8\%\,cm^2/s$. Bars represent average experimental error for SEM-EDX measurements. Experimental data corresponds to visual observations of the eggshell thickness using SEM-EDX.

at 4, 5 and 12 s impregnation times (Table 4). This demonstrates that the impregnation process for catalysts of the series 2cP-01-W is being controlled by diffusion and it can be represented using the model of Eq. (19).

6. Conclusions

1. A successful methodology is presented in this study to produce eggshell catalysts.
2. It is shown that parameters such as impregnation time, metal solution concentration, solution viscosity, as well

as state of the support before impregnation strongly affect the evolution of the thickness and the final state of the metal in the eggshell catalyst.

3. It is demonstrated that the wet impregnation, using low metal concentration solutions produces a more progressive eggshell profile than the dry impregnation.
4. Modeling of the impregnation process is used to describe both the dry impregnation effected with low and high metal concentration solutions, as well as the wet impregnation effected with low metal concentration solutions.
5. These models include either no adjustable parameter (dry impregnation) or a single adjustable parameter (wet impregnation) providing adequate descriptions of the eggshell catalysts formation process.

References

[1] E. Iglesia, S. Soled, J. Baumgartner, S. Reyes, J. Catal. 153 (1995) 108–122.
[2] M. Komiyama, Catal. Rev.-Sci. Eng. 27 (1985) 273–341.
[3] S. Minhas, J.J. Carberry, J. Catal. 14 (1969) 270–272.
[4] C. Horvath, J.M. Engasser, Ind. Chem. Eng. Fudam. 12 (1973) 229.
[5] S.Y. Lee, R. Aris, Catal. Rev.-Sci. Eng. 27 (1985) 207–340.
[6] M. Komiyama, Catal. Rev.-Sci. Eng. 27 (1985) 341–372.
[7] R. Maatman, C. Prater, Ind. Eng. Chem. 49 (1957) 253.
[8] A. Gavriilidis, A. Varma, M. Morbidellis, Catal. Rev.-Sci. Eng. 35 (3) (1993) 399–456.
[9] K. Yeung, A. Gavriilidis, A. Varma, M. Bashin, J. Catal. 174 (1998) 1–12.
[10] W.H. Zimmerman, J.A. Rosin, D.B. Bukur, Ind. Eng. Chem. Res. 28 (1989) 406–413.
[11] E. Peluso, Master of Eng. Sci., University of Western Ontario, Canada, 1998.
[12] M. Komiyama, R.P. Merrill, Bull. Chem. Soc. Jpn. 54 (1984) 1169–1173.
[13] R.C. Vincent, R.P. Merrill, J. Catal. 35 (1974) 206–217.
[14] E. Peluso, C. Galarraga, H. de Lasa, ISCRE 16, Chem. Eng. Sci., 2000, in press.
[15] C. Galarraga, E. Peluso, H. de Lasa, Stud. Surf. Sci. 130 (2000) 395–400.
[16] H. Carslaw, J. Jaeger, Conduction of Heat in Solids, Oxford University Press, Oxford, 1959, p. 504.
[17] C. Galarraga, Master of Eng. Sci., University of Western Ontario, Canada, 1998.
[18] S.W. Ho, M. Houalla, D. Hercules, J. Phys. Chem. 94 (1990) 6396–6399.
[19] L.L. Hegedus, T.S. Chou, J.C. Summers, N.M. Potter, in: Proceedings of the 2nd Int. Symposium on Scientific Basis for the Preparation of Heterogeneous Catalysts, 1979, p. 171.