Supplementary Data

Appendix A

Upon dry impregnation, replacement of fluid inside the pore space (called capillary) by impregnation solution takes place through the action of capillary forces. Figure A. 1 shows a schematic picture of a cylindrical pore with radius R_{pore} in contact with the impregnation solution.



Figure A. 1 - Capillary in contact with wetting fluid

The evolution of the distance travelled by the liquid into the pore (z) as a function of time (t) depends on three different forces: capillary force, $\vec{F}_{capillary}$, friction force, $\vec{F}_{friction}$ and gravity force, \vec{P} , which is negligible compared to the first ones [1].

The formation of bubbles that can occur in closed end pores was neglected (the gas phase is supposed to evacuate instantly from the pores).

The following paragraphs explain how to obtain z(t) based on Washburn model.

The linear momentum balance with respect to a control volume is given by the following equation [1]:

(Sum of forces acting on control volume) = (Rate of momentum out of control volume) - (Rate of momentum into control volume) + (Rate of accumulation of momentum within control volume)

Recalling the conservation of linear moment and Newton's second law, Eq. A. 1 results in:

$$\sum \vec{F} = \frac{d(m, \vec{v})}{dt}$$
 Eq. A. 2

Where,

 $\Sigma \vec{F}$ is the sum of forces acting on control volume,

m corresponds to mass,

 \vec{v} corresponds to velocity

t stands for time.

The evolution of the solution front is a result of capillary and friction forces Eq. A. 2 can be written as:

$$\frac{d(m.\vec{v})}{dt} = \vec{F}_{capillary} + \vec{F}_{friction}$$
Eq. A. 3

Capillary force applied in the cross section (S) of the cylindrical pore is based on Young-Laplace equation $(\Delta P_{Laplace})$ and is defined in Eq. A. 4.

$$F_{capillary} = \Delta P_{Laplace} \cdot S = \frac{2 \cdot \gamma \cdot cos\theta}{R_{pore}} \cdot \pi \cdot R_{pore}^2 \leftrightarrow$$
 Eq. A. 4

$$F_{capillary} = 2 \cdot \pi \cdot R_{pore} \cdot \gamma \cdot \cos\theta \qquad \text{Eq. A. 5}$$

Where,

 R_{pore} stands for the pore radius,

 γ is the interfacial tension,

 θ is the wetting angle of the wetting fluid on the surface of the capillary.

To define the **friction force**, a linear momentum balance within the control volume schematized in Figure A. 2, which represents the section of a cylindrical tube of radius R and length L is required. The following assumptions are adopted [51]:

- Incompressible, continuous, Newtonian and viscous fluid flowing at steady state within a cylindrical tube
- Fully developed fluid, which means that velocity profile does not change along the flow direction (in this case, z)



Figure A. 2 - Control volume for a flow within a cylindrical tube of radius R [51]

The momentum balance equation is based on Eq. A. 1. Since the velocity profile does not change along z direction, the resulting force acting on the system is zero. This resulting force is composed of:

 Viscous friction forces (related with shear stress tensor τ), due to radial motion of momentum at a molecular scale

- Pressure forces (P) exerted at the extremities
- Gravity force, which is negligible compared to the first ones [51]

Additionally, the accumulation term is also zero.

Therefore, the linear momentum balance with respect to the control volume schematized in Figure A. 2 is given in Eq. A. 6.

$$(P_1 - P_2) \cdot 2 \cdot \pi \cdot r \cdot dr + 2 \cdot \pi \cdot r \cdot z \cdot \tau - 2 \cdot \pi \cdot (r + dr) \cdot z \cdot (\tau + d\tau) = 0$$
 Eq. A. 6

With,

$$\tau + d\tau = \tau + \frac{d\tau}{dr}dr$$
 Eq. A. 7

Rearranging Eq. A. 6 the following relation (Eq. A. 8) is obtained, where $\Delta P_{friction} = P_1 - P_2$:

$$d(r \cdot \tau) = \frac{\Delta P_{friction} \cdot r \cdot dr}{L}$$
 Eq. A. 8

Where,

$$\tau = \frac{\Delta P_{friction} \cdot r}{2L} + \frac{Cte}{r}$$
 Eq. A. 9

The first boundary condition is given by:

 $r = 0: \tau \neq \infty$

Thus, shear stress is defined in the following equation.

$$\tau = \frac{\Delta P_{friction} \cdot r}{2L}$$
 Eq. A. 10

This relation is valid for all viscous fluids in laminar flow in a cylindrical tube. As one of the hypothesis stated is that the fluid is a Newtonian one, the shear stress is given by:

$$\tau = -\mu \cdot \frac{dv}{dr}$$
 Eq. A. 11

Where,

 μ is the shear viscosity of the fluid

dv/dr is the velocity gradient that corresponds to the deformation rate of a fluid element.

Combining Eq. A. 10 and Eq. A. 11 and integrating between radius, r and pore radius, R_{pore}:

$$\int_{v_r}^{v_{wall}} dv = \int_r^{R_{pore}} -\frac{\Delta P_{friction} \cdot r \cdot dr}{2 \cdot \mu \cdot z}$$
 Eq. A. 12

To solve integral given by Eq. A. 12, a second boundary condition is necessary.

$$r = R_{pore}$$
: $v = 0$

Therefore, Eq. A. 12 gives:

$$v(r) = \frac{\Delta P_{friction}}{4 \cdot \mu \cdot z} \cdot \left(r^2 - R_{pore}^2\right)$$
 Eq. A. 13

The average velocity is given by:

$$\bar{v} = \frac{\int_0^{2\pi} \int_0^R v(r) \cdot r dr d\theta}{\pi R^2}$$
 Eq. A. 14

Hence, the average velocity results in Eq. A. 14, which corresponds to Hagen-Poiseuille equation that relates the average flow velocity with the pressure drop due to friction.

$$\bar{v} = \frac{\Delta P_{friction} \cdot R_{pore}^2}{8 \cdot \mu \cdot z}$$
 Eq. A. 15

Finally, friction force (F_{friction}) applied in the cross section (S) of the cylindrical pore is defined in Eq. A. 16:

$$F_{friction} = \Delta P_{friction} \cdot S \Leftrightarrow$$

$$F_{friction} = 8 \cdot \pi \cdot \mu \cdot z. \, \bar{v}$$
Eq. A. 16

The friction force is more important as velocity increases. It is also proportional to the length z of the tube. Eq. A. 17 is then used to calculate the capillary impregnation dynamics, in which \bar{v} represents the penetration rate, which is given by the following equation:

$$\bar{v} = \frac{dz}{dt}$$
 Eq. A. 17

Washburn model [2] is used to calculate the penetration rate. This model is valid for low Reynolds number (Re < 1) and viscous fluid. It is also assumed that the flow of the impregnation solution in the pore is characterized by Poiseuille steady stated. Therefore, the small inertia effects are neglected. According to Washburn model, becomes:

$$\frac{d(m.\vec{v})}{dt} = \vec{F}_{capillary} + \vec{F}_{friction} = 0$$
 Eq. A. 18

Combining Eq. A. 5, Eq. A. 16 and Eq. A. 18, one obtains:

$$2 \cdot \pi \cdot R_{vore} \cdot \gamma \cdot \cos\theta - 8 \cdot \pi \cdot \mu \cdot z. \, \bar{v} = 0$$
 Eq. A. 19

Combining Eq. A. 17 and Eq. A. 19, it results:

$$\frac{dz^2}{dt} = \frac{R_{pore} \cdot \gamma \cdot \cos\theta}{2 \cdot \mu}$$
 Eq. A. 20

Assuming that z(0) = 0, the distance z that the impregnation solution travels into the pore is given by:

$$z = \sqrt{\frac{R_{pore} \cdot \gamma \cdot \cos\theta}{2 \cdot \mu}} \cdot t$$
 Eq. A. 21

[1] N. Midoux, Mécanique et rhéologie des fluides en génie chimique, Tec & Doc, 1993.

[2] E.W. Washburn, The Dynamics of Capillary Flow, Physical Review 17 (1921) 273-283

Appendix B

In order to validate the metal distribution profiles observed by ¹H MRI, the same impregnated samples were characterized by EPMA technique. To this end, the radial intensity profiles of MRI images and the average metal concentration profiles obtained by EPMA were compared. The radial intensity profiles as a function of the distance from the edge of the support were obtained through image processing as described in [3]. These profiles were then corrected by a constant factor in order to take into account the relaxation times dependence as well as by a scaling factor applied by the MRI software in each image, as described in the following paragraphs.

First, the software ImageJ is used to export MRI image data into 16bit.tiff files. From these data, an IFPEN software for image processing [4] is used to calculate on each image the radial intensity profiles as a function of the distance from the edge of the support. For each distance, a minimum, a maximum and an average intensity are computed, and provide associated profiles. In this study, the measured intensity profiles are referred as the apparent intensity (I) profiles as they do not take into account neither relaxation times dependence nor normalization carried out by Paravision software.

These apparent intensity profiles (I) are corrected with K factor (see Eq. B. 1 [5]) in order to take into account the relaxation times dependence.

$$I = I_0 K Eq. B. 1$$

In Eq. B. 1, I_0 is the signal that would be measured immediately following a 90° pulse and K is defined according to Eq. B. 2:

$$\mathbf{K} = \mathrm{e}^{-\mathrm{t}_{\mathrm{p}}/T_{2}^{*}} G(\frac{TR}{T_{1}}, \alpha) \qquad \qquad \mathbf{Eq. B. 2}$$

Where t_p corresponds to the encoding time, T_2^* corresponds to the transverse relaxation and $G(TR/T_1, \alpha)$ describes the signal attenuation from the Ernst-angle excitation pulse, α (see Eq. B. 3).

$$G = \frac{1 - E}{1 - E^2} \sin(\alpha)$$
 Eq. B. 3

Where,

$$\cos(\alpha) = E = e^{-TR/T_1}$$
 Eq. B. 4

In Eq. B. 4, TR corresponds to the repetition time and T_1 corresponds to the longitudinal relaxation.

Additionally, the apparent intensity profiles (I) are also corrected by the scaling factor of each image applied by Paravision software (Visu Core Data Slope parameter). The mathematical equation to obtain average radial intensity profiles (I_0) is shown in Eq. B. 5.

$$I_0 = \frac{I \times Scaling \ factor}{K}$$
 Eq. B. 5

The comparison between average concentration profiles obtained by EPMA and the corrected radial intensity profiles (I_0) obtained by MRI is shown in Figure B. 1. The shaded area delimits the maximum and minimum radial intensity profiles. Both techniques show the presence of nickel ions in the same positions of the catalyst pellet regarding the spatial resolution of each technique. Slight differences may be observed due to the signal to noise ratio of MRI images, since the sensitivity of MRI technique is lower than EPMA. Yet, no quantitative information about the evolution of the concentration profile of nickel ions inside the pellet can be obtained through this approach.





alumina pellet at equilibrium state after dry impregnation corresponding to approximately (a) 12h in the case of with 0.05M $[Ni^{2+}]$ solution and (b) 30 min in the case of 0.2M $[Ni^{2+}]$ solution. Shaded area delimits the maximum and minimum radial intensity profiles (I₀).

[3] L. Catita, A.-A. Quoineaud, D. Espinat, C. Pichon, O. Delpoux, Impact of Citric Acid on the Impregnation of CoMoP/γ-Al2O3 Catalysts: Time and Spatially Resolved MRI and Raman Imaging Study, Topics in Catalysis (2018) 1474–1484.

[4] M. Moreaud, F. Cokelaer, Flowing Bilateral Filter: Definition and Implementations, Image Anal Stereol 34 (2015) 101–110.

[5] S. Gravina, D.G. Cory, Sensitivity and Resolution of Constant-Time Imaging, Journal of Magnetic Resonance, Series B 104 (1994) 53–61.

[6] P. Thévenaz, T. Blu, M. Unser, Interpolation revisited, IEEE Transactions on Medical Imaging 19 (2000) 739–758.

Appendix C



Figure C. 1 - Evolution of advancing front of water calculated from **Erreur ! Source du renvoi introuvable.**) as a function of time: z corresponds to the distance travelled by liquid into the pore (m) and R_p to the porous radius (m)

Appendix D



Figure D.1 - Influence of the parameters (a) q_t and (b) K_{ads} on the objective function (see Erreur ! Source du renvoi

introuvable.)