

Mean penetration depth of metals in hydrodemetallation catalysts



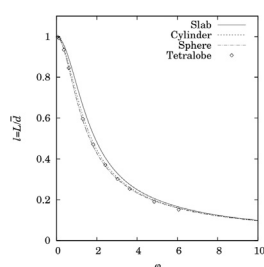
Loïc Sorbier*, Frédéric Bazer-Bachi, Maxime Moreaud, Virginie Moizan-Basle

IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

HIGHLIGHTS

- We propose a descriptor to measure the deposit depth of metal in used HDM catalyst.
- It is well defined even for industrial complex grain shapes.
- It uses the distance transform of the shape of the catalyst grain.
- It may be linked to catalyst efficiency through a simple model of metal deposit.

GRAPHICAL ABSTRACT



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ABSTRACT

A descriptor has been proposed, the mean penetration depth, to characterize the deposit profiles of metals in hydrodemetallation catalysts. This mean penetration depth can be obtained from concentration maps or profiles of elements along catalyst cross sections using local characterization techniques. This descriptor is well suited even for very irregular shapes such as multilobed extrudates often encountered in industrial catalysts. Using a very simple model of metal deposit, the mean penetration depth can be analytically related to the Thiele modulus of the deposit reaction and consequently to the catalyst efficiency for trivial shapes (infinite slab, infinite cylinder and sphere). The mean distance to the surface of the catalyst pellet is found to be the convenient quantity to renormalize Thiele modulus and mean penetration depth to obtain an universal curve independent of the catalyst pellet shape. An example of application is given on a used hydrodemetallation catalyst of tetralobed shape.

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1. Introduction

Hydroprocessing of oil residues is an industrial process, expected to be of growing importance with the rarefaction of light crudes, the increasing demand for middle distillates and harsher specification on sulfur contents of end products [Merdrignac et al. \(2013\)](#). This process begins with metal impurities removal to protect downstream catalysts. The main metallic impurities in crude oil are vanadium and nickel and their concentrations can reach tens to hundredth ppm. This removing of metals is performed in fixed or ebullated beds by dedicated hydrodemetallation (HDM) catalysts under high hydrogen

pressure. HDM catalysts are typically millimeter sized alumina extrudates, containing transition metal sulfides as the hydrogenating active phase. They have an extruded shape with a multilobed (tri-lobed, tetralobe) cross section. Most of the metals are contained in a fraction called asphaltenes consisting of high molar mass polyaromatic species [Mullins \(2010\)](#). The deposition of the metal is often done under internal diffusional limitation leading to hollow deposition profiles of metals on spent catalysts. The removal kinetics is a first order one for nickel and half order one for vanadium [Callejas and Martínez \(1999\)](#). The deposition of metals implies a progressive plugging of the porosity up to the percolation threshold where apparent activity falls dramatically down and catalyst needs to be replaced. The percolation threshold for porosity is the smallest porosity where a connected porous network has a size at least equal to the

* Corresponding author.

E-mail address: loic.sorbier@ifpen.fr (L. Sorbier).

Nomenclature

c	local concentration of deposited metal in catalyst, wt%	l	normalized mean penetration depth of metal, dimensionless
c_p	concentration of metal precursor in liquid, kg/m ³	L	mean penetration depth of metal, m
c_0	concentration in liquid at the surface of the pellet, kg/m ³	R	radius of the ball in \mathbb{R}^n , m
C	global concentration of deposited metal in catalyst, wt%	S	external surface of the pellet, m ²
d	distance to the border of the pellet, m	V	volume of the pellet, m ³
\bar{d}	mean distance to the border of the pellet, m	ε	pellet's porosity, dimensionless
D_e	effective diffusion coefficient of metal precursor in pellet, m ² /s	η	catalyst efficiency, dimensionless
k	first order rate constant of metal removal, s ⁻¹	ϕ	Thiele modulus, dimensionless
		φ	normalized Thiele modulus, dimensionless
		ρ	structural volumetric mass of the catalyst pellet, kg/m ³

pellet's size. Below this point, it is clear that the transport of reactants and products in the whole pellet is no longer possible Sahimi et al. (1990). The percolation threshold of the porosity induced by a random solid sphere model is close to 0.054 Jeulin (2012). As long as the local catalyst porosity is far above this threshold, pore plugging is progressive. Thus, taking into account the percolation threshold is particularly important for predicting the end of life of the catalyst.

The characterization of spent HDM catalysts is useful to study the influence of process operating condition, the metal deposition mechanism and predict the catalyst life time Furimsky and Massoth (1999). A lot of work has been published on vanadium and nickel profiles on HDM spent catalyst. Toulhoat et al. have shown that a macro-mesoporous supports leads to much less hollow profiles than purely mesoporous ones Toulhoat et al. (1990). Agrawal and Wei have observed different metal profiles along the reactor during vanadium and nickel porphyrins hydroprocessing Agrawal and Wei (1984). Others have shown that nickel profiles are much more flat than the vanadium ones Kobayashi et al. (1987), Callejas et al. (2001), Marafi et al. (2007). Experimental metal deposit profiles are often used as a qualitative validation of a complex deposit reactor model taking into account pore plugging and chemical heterogeneity of oil residues Arbabi and Sahimi (1991), Zhang and Seaton (1996), Toulhoat et al. (2005), Vogelaar et al. (2006), Verstraete et al. (2007), Marafi et al. (2010).

One paper tackled the relationship between metal deposition profile and catalyst efficiency Tamm et al. (1981). On cylindrical extrudates, Tamm et al. compute the global concentration of metal in the pellet and the surface concentration. Catalyst efficiency is simply the ratio of these two quantities. Unfortunately, this approach does only hold for long cylindrical extrudates which raises the question on how to apply it for real industrial multi-lobed extrudates Callejas et al. (2001).

The main goal of this paper is thus to propose a new descriptor that will allow us to link the metal deposition profiles and catalyst efficiencies for any pellet shape. The paper is organized as follow. In the first section, we define a quantitative criterion, the mean penetration depth L , to characterize the deposit of metals in the pellet. We derive the simplest model of metal deposition that will allow us to calculate analytical expression of the mean penetration depth for trivial shapes (infinite slab, infinite cylinder, sphere). We give numerical methods to compute L either from two-dimensional concentration map or from profiles along a cross-section of an extrudate. The second section gives the results of the calculations and shows that a proper scaling of L and Thiele modulus allows to obtain a universal curve nearly independent of the pellet's shape. A concrete example of application is given on a spent HDM catalyst with a tetralobed shape. In the third section, we discuss the applicability and limits of our approach and compare experimental results with available data found in literature before giving our conclusions.

2. Materials and methods**2.1. Simple metal deposit model**

The simplest model of metal deposit implies an unique metal precursor, reacting with a first order reaction with kinetic constant k and diffusing in the catalyst pellet following a Fick law with effective diffusion coefficient D_e . Assuming that the catalyst grain is isothermal and there is no pore plugging, the steady state concentration of the metal precursor c_p obeys the following equation:

$$D_e \nabla^2 c_p - k c_p = 0 \quad (1)$$

With Dirichlet boundary condition at the border of the grain:

$$c_p(\mathbf{x}) = c_0 \quad \forall \mathbf{x} \in \partial G \quad (2)$$

where ∂G is the border of the grain G and c_0 the concentration in liquid phase outside the grain that is supposed homogeneous, neglecting external transfer limitations. Neglecting the deposition of metal during the transient regime, the mass d^2m deposited during the time interval dt in a volume dV is equal to:

$$d^2m = k c_p(\mathbf{x}) \varepsilon dt dV \quad (3)$$

where ε is the internal porosity of the pellet. Neglecting pore plugging (ε is constant), the mass dm deposited in a volume dV after a time t is equal to:

$$dm = \varepsilon k t c_p dV \quad (4)$$

Assuming that $dm \ll (1 - \varepsilon) \rho dV$, otherwise said, few metal has been deposited which is compatible with neglecting pore plugging, the local deposited metal mass concentration $c(\mathbf{x})$ is equal to:

$$c(\mathbf{x}) = \frac{\varepsilon k t}{(1 - \varepsilon) \rho} c_p(\mathbf{x}) \quad (5)$$

where ρ is the structural density of the pellet. Under these very simple assumptions, the local metal deposit concentration is proportional to the steady state concentration of the metal precursor. This model is very naive and much more simple than reactor level models taking into account pore plugging, correct kinetic order of deposit and heterogeneity of metal precursors. Its simplicity will allow the analytical computation of the mean penetration depth of metals and efficiency at the grain scale.

The catalyst efficiency η is defined as the rate of precursor conversion in the whole pellet over the conversion on the same pellet obtained without internal diffusion limitation Davis and Davis (2012). Under the above assumption, catalyst efficiency is simply equal to the ratio of global concentration C in the pellet over the concentration at the border c_0 :

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