Application of a three-stage approach for modeling the complete period of catalyst deactivation during hydrotreating of heavy oil

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HIGHLIGHTS

- Catalyst deactivation due to hydrotreating reactions was studied.
- A three-stage deactivation model was employed.
- Simulations of loss of catalyst activity was carried out at SOR, MOR and EOR.
- Different deactivation patterns were observed depending on HDT reaction.

ARTICLE INFO

ABSTRACT

Modeling the catalyst deactivation due to hydrodeasphaltenization (HDAsph), hydrodemetallization (HDM) and hydrodesulfurization (HDS) reactions with time-on-stream (TOS) was carried out by using a model that considers three deactivation stages: start-of-run (SOR), middle-of-run (MOR) and end-of-run (EOR). Experimental data of kinetics, intra-particle mass transfer and conversion affected by deactivation phenomena were obtained from laboratory scale reactor. Loss of activity was studied at constant operating conditions of temperature, pressure, liquid hourly space velocity (LHSV) and H$_2$-to-oil ratio for a range of time-on-stream. It is found that different deactivation patterns are obtained depending on the considered reaction. It is predicted that catalyst exhibits higher rate of deactivation for HDS than for HDM at long TOS.

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1. Introduction

Fixed-bed is the most preferred for hydrotreating processes due to a number of advantages over other reactor types [1]. However when processing heavy oils and residua its main disadvantage is the catalyst deactivation due to metals and coke deposition mainly, which is more dramatic at high severity conditions and long time-on-stream [2].

At start-of-run (SOR) deactivation of catalyst is primary related to hydrocracking reaction when processing heavy oil. At that stage, considerable loss of activity occurs due to coke deposits on catalyst surface. It is found that a pseudo-steady state deactivation catalyst is reached at the end of SOR for hydrocracking reaction due to equilibrium between deposited and dissolved coke [3,4], although for longer TOS the nature of coke changes toward insoluble deposits. Deactivation of sites for vanadium removal also can occur at short TOS due to deposits of such a metal on catalyst at very low amounts [5,6].

Heavy crude oils have high contents of impurities such as vanadium, sulfur and nickel mainly. Metals particularly, cause permanent irreversible deactivation at middle and long TOS (100–3000 h+) in different ways due to deposition on surface catalyst [7]. The deposits tend to grow with TOS blocking the pore mouths, reducing the pore diameter and lowering consequently its activity at such levels that unavoidable unit shut down is carried out. In fact, it is reported that when catalyst activity is reduced at 20–30% of its original value it has been replaced [8].

Sulfur is the main impurity that must be removed from fuels derived from unconventional crudes. Because the most refractory sulfur compounds are contained in heavy complex molecules, it is necessary to destroy firstly those big molecules to remove the heteroatom.

Studying the deactivation phenomena due to HDT reactions is a very complex task from technical point of view. Also, because of the extremely high costs of experiments and time consuming, to estimate the performance and life of catalysts under deactivation effects is desirable to account for a model that simulates the deactivation patterns toward HDT reactions at long time-on-stream.

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Nomenclature

C	species concentration
D_0	initial diffusion coefficient within pore catalyst
d_p	catalyst particle diameter
D_t	diffusion coefficient within pore catalyst
EOR	end-of-run
e	the basis of natural logarithm
k_i	reaction rate constant
MOR	middle-of-run
N	total concentration of sites available for any particular reaction
N_i	concentration of any active sites at any time
N_i^0	concentration of any active sites at initial time-on-stream
N_1	concentration of sites type I
N_2	concentration of sites type II
SOR	start-of-run
TOS	time-on-stream
t	variable for time-on-stream
t_∞	catalyst life

Superscripts

app	apparent

Subscripts

f	related to feed conditions
in	intrinsic
p	product

Greek letters

α_1	rate constant of diminution on sites concentration type I
α_2	rate constant of diminution on sites concentration type II
β	proportional constant in Eq. (21)
Δ	symbol for difference
ϕ	Thiele modulus
η	overall effectiveness factor
η_0	initial effectiveness factor
η_t	effectiveness factor affected by diffusional resistances
φ	overall activity coefficient
φ_A	deactivation function of active sites
φ_D	deactivation function due to deposits

Various catalyst deactivation models have been reported in the literature for modeling the deactivation at start-of-run and middle-of-run by separate [9,10]. However very few reports deal with modeling the three-stages together [8,9,11]. Some models that account for the three stages of deactivation do not include the main hydrotreating reactions occurred during heavy petroleum processing, but only a single reaction. On the other hand, complex deactivation models have been developed for model molecules mainly, and some conclusions derived from these approaches cannot be straightly extrapolated to deactivation of catalyst employed for hydrotreatment of real complex feedstock [12]. When using complex models for HDT of real feedstock a number of constants need to be estimated from experimental information, and such parameters change as experimental conditions do, so that not really advantage can be taken from it than using simple models.

The aim of this work is to apply a simple deactivation model that considers the three stages of deactivation, i.e. SOR, MOR, and EOR, to simulate the catalyst decay occurring during the main hydrotreating reactions of heavy oil in an isothermal bench–scale plant. Experiments at SOR are used to predict the deactivation profile at MOR based on initial trend.

2. Deactivation model

2.1. Assumptions

The model used in this work allows accounting for the three stages of catalyst deactivation. It was derived by Idei et al. [13–16]. The following assumptions were considered:

 I. There are different active sites in the catalyst selective for HDT reactions.
 II. Deactivation of any type of sites is independent from the others.
 III. Each HDT reaction is carried out in two types of sites: sites type I which are deactivated at a fast rate and sites type II that correspond to those that are deactivated slower than sites type I.

 IV. The rate of loss of any type of sites is proportional to its concentration.
 V. The concentration of any type of sites is proportional to reaction rate constant of species that reacts on such sites.
 VI. First reaction order.
 VII. There is no activity profile along the catalyst bed.

2.2. Development of deactivation model: absence of diffusional resistances due to deposits

If N_i is the concentration of any type of active sites in the catalyst, its rate of diminution is proportional to the concentration of corresponding species. For sites type I it can be written that:

$$-\frac{dN_1}{dt} = \alpha_1 N_1 \tag{1}$$

Similar equation for loss of sites type II can be written:

$$-\frac{dN_2}{dt} = \alpha_2 N_2 \tag{2}$$

Because of assumption II, both Eqs. (1) and (2) can be solved independently with the following initial conditions:
At $t = 0$, $N_i = N_i^0$

Thus, after proper substitution of conditions the solutions for Eqs. (1) and (2) are:

$$N_1 = N_1^0 e^{-\alpha_1 t} \tag{3}$$

$$N_2 = N_2^0 e^{-\alpha_2 t} \tag{4}$$

If $N = N_1 + N_2$ one arrives at:

$$N = N_1^0 e^{-\alpha_1 t} + N_2^0 e^{-\alpha_2 t} \tag{5}$$

where N represents the total concentration of sites available for any particular reaction.

It is assumed that initial concentration of sites I and II is, according with Eq. (5):

$$N^0 = N_1^0 + N_2^0 \tag{6}$$

The deactivation function of active sites φ_A is defined as: