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Modeling initial decay of hydrodemetallization catalyst with simultaneous adsorption and reaction mechanism

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Abstract

Two mechanisms, a classical poisoning mechanism of the metal deposits and a simultaneous adsorption and reaction mechanism newly proposed in our preceding study, are applied to model the performance of two hydrodemetallization (HDM) catalysts in the aging experiments with Venezuelan vacuum residue. By interpreting the initially decaying activity as an effect of decreasing adsorption on alumina supports rather than deactivation of original active sites, the new model follows the trends of the observations much better. Moreover, the typical characteristics of the poisoning model with autocatalytic effects are also part of the new model: the initial stage of decaying is related to the metal concentrations of the feed and the monolayer coverage capacity of the catalyst, and after this period there is a residual activity left. Therefore, the simultaneous adsorption and reaction mechanism is good and convincing enough to explain the initial decay of the HDM catalysts with real petroleum feeds.

Keywords: Hydroprocessing; Hydrotreating; Hydrodemetallization; HDM; Catalyst deactivation; Initial decay of HDM catalysts; Modeling; Alumina support; Adsorption on alumina; Poisoning of metal deposits

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1. Introduction

Hydrodemetallization (HDM) is an important step in industrial catalytic hydroprocessing of residual oils. During the operation, HDM catalysts undergo a decay of the apparent activity, which is characterized by an S-shape temperature versus time-on-stream curve with three distinct periods [1,2]. The decreasing activity has been extensively studied and reviewed in the literature as a result of catalyst deactivation, which is commonly ascribed to the accumulation of carbonaceous and metal deposits on the surface [3–5]. No doubt, a large quantity of deposits will substantially influence the diffusional properties of the porous catalysts so as to restrict access to the pore system finally, which is generally thought to be responsible for the deactivation of the last two stages. Nevertheless, there has been considerable controversy on what kind of mechanisms and to what extent each deposit contributes to the initial dramatic decay of the catalysts [1,6–8]. Meanwhile, various models that combine mass-transfer effects with proposed deactivation mechanisms have been developed to characterize the process for predicting catalyst deactivation under commercial operation conditions. They differ in the mechanism of deactivation, in the kinetics of reaction, and in the description of diffusivity or pore structures [1,2,9–20]. Notably, since a stationary coke level on the catalyst is readily established in most industrial operations, the majority of the models utilize the deposited metals as an index of catalyst aging even at the early stage.

In our preceding study using model compounds, a new mechanism was proposed for the initial decline of the HDM catalyst [21]. Rather than a result of catalyst deactivation, the initial apparent activity was demonstrated to be an effect of a nearly constant catalytic activity of the active phase coupled with an extra decreasing adsorption on the alumina support when the available sites were gradually and continuously occupied. Subsequently, the simultaneous adsorption and reaction mechanism was used to model the time-course conversions of metalloporphyrins in a fixed-bed reactor under a constant reaction temperature and fit the experimental data reasonably well. The objective of this study is to ascertain whether the new mechanism is applicable to the HDM process with real petroleum feeds. For comparison, the clas-

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sical poisoning mechanism of the metal deposition is also included to model the performances of two HDM catalysts in the accelerated aging experiments with Venezuelan vacuum residue.

2. Experimental and mathematical methods

A laboratory-prepared NiMo/fibrillar alumina catalyst F-145 and a commercial CoMo/Al_2O_3 HDM catalyst (Haldor Topsoe TK-710) were aged in previous studies of our group for about 530 and 1400 h, respectively [22,23]. The experiments were performed in a down-flow trickle-bed reactor at 11 MPa of total pressure and a constant reaction temperature (643 K) using Venezuelan vacuum residue that contained as high as 576 ppm metals (Ni + V). Catalyst F-145 originally in the form of 1-mm cylindrical extrudates had been grounded and sieved with 0.5- to 1.0-mm screens before use. So in the modeling, F-145 was approximately treated as a spherical pellet with an equivalent diameter of 0.75 mm, while TK-710 was regarded as an infinite cylinder with a diameter of 0.8 mm. The liquid hourly space velocity (LHSV) was 0.75 h^{-1} for both of the runs, and the bed void fraction was 0.53 for F-145 and 0.41 for TK-710. The other details about the experiments were introduced in Refs. [22,23].

When the simultaneous adsorption and reaction mechanism was applied to model the performances of the catalysts, a power-law rate expression was chosen for the reaction and a nonlinear Langmuir isotherm was thought favorable to the adsorption in this work. The details of the mathematical methods with the simultaneous adsorption and reaction mechanism can be found in the preceding study [21].

As for the poisoning mechanism of the metal deposition, the basic assumptions were as follows: separate rate forms to express the kinetics of the primary reaction and the deactivation process; power-law expressions for the reaction and deactivation kinetics; pseudo-steady state of the catalyst particles. And then for an isothermal particle when film mass-transfer resistance is negligible and pore diffusion is dominate, the differential pseudo-steady-state mass balance for the fluid concentration within the particle C_i yields

$$D_e\left(\frac{d^2C_i}{dr^2}+B(r)\frac{dC_i}{dr}\right)=k_iS_a\rho_cC_i^n a, \tag{1}$$

$$-\frac{da}{dt}=k_dC_ia^m, \tag{2}$$

with initial and boundary conditions

$$a=1;\quad t=0;\quad R\geqslant r\geqslant 0, \tag{3}$$

$$C_i=C_b;\quad t\geqslant 0;\quad r=R, \tag{4}$$

$$\frac{\partial C_i}{\partial r}=0;\quad t\geqslant 0;\quad r=0. \tag{5}$$

For a spherical pellet $B(r)=2/r$, and for an infinite cylinder $B(r)=1/r$. In the equations, D_e represents the effective diffusivity, r is the radial coordinate of the particle and R is the radius, ρ_c is the density of the particle, S_a denotes the surface area per unit mass of the particle, k_i is the rate constant of the intrinsic reaction, n is the surface reaction order, a denotes the fractional activity of the catalyst that is a function of the process time t, k_d is the rate constant of the intrinsic deactivation, m is the deactivation order, and C_b is the bulk stream concentration of the species.

The set of Eqs. (1) and (2) is a two-point boundary value problem, which was solved numerically in this study by using the finite element method (FEM) on commercial software MATLAB 5.3. The results are expressed in the form of concentration profiles $C_i(t,r)$ and concentration gradients $(\partial C_i/\partial r)(t,r)$ inside the particle at different times on stream. Thus, an "initialized" effectiveness factor of the deactivating particle [24] can be calculated according to

$$\eta_t=\frac{g}{R}\frac{D_e}{k_iS_a\rho_cC_b^n}\frac{dC_i}{dr}\bigg|r=R, \tag{6}$$

where g is a constant that is equal to 3 for a spherical pellet and 2 for an infinite cylinder.

With the results of a single particle, we now consider the case that the disappearance of the species takes place in a plug-flow fixed bed with no concentration gradients along the bed under a steady and isothermal state. The advantage of using the time-dependent effectiveness factor is that it is easily incorporated in the reactor design equation to predict reactor performance under the combined influence of the deactivation and diffusion [24]. If the axial dispersion is negligible, the differential equation of the material balance for the bed is given by

$$-\frac{v_0}{A_c}\frac{dC_b}{dz}=k_iS_a\rho_bC_b^n\eta_t, \tag{7}$$

where v_0 denotes the volumetric flow rate, A_c and z are the cross-sectional area and the axial position of the bed, respectively, and ρ_b is the density of the bed.

If C_0 denotes the feed concentration of the species, with the aid of the boundary condition at the entrance of the reactor,

$$C_b=C_0\quad \text{at } z=0. \tag{8}$$

Equation (7) can be integrated to give the concentration of the species at the bed exit C_{out}, and the corresponding conversion X is calculated according to the definition

$$X=\frac{C_0-C_{out}}{C_0}\times 100\%. \tag{9}$$

Subsequently, the parameters that characterize the proposed mechanism under restrictive diffusion were estimated by fitting the corresponding model into the experimental data using the least-squares method on MATLAB.

3. Results an discussion

The catalyst performances in the aging experiments are presented in Figs. 1 and 2, in which the demetallization

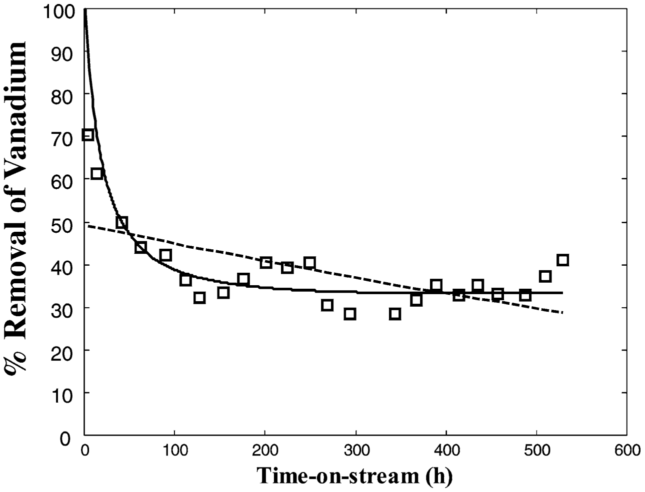

Fig. 1. Experimental and modeling results of catalyst F-145. Symbol (□) represents the experimental results from Ref. [22]. The solid line is the modeling results using the simultaneous adsorption and reaction mechanism with first-order reaction. The dashed line is the modeling results using the poisoning mechanism with the first-order reaction and deactivation.

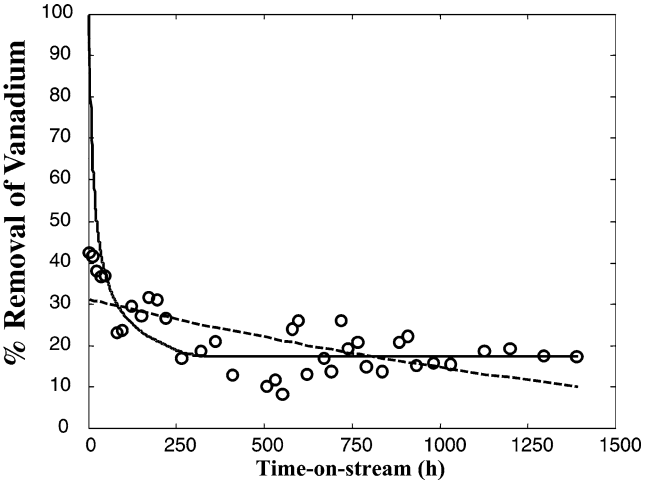

Fig. 2. Experimental and modeling results of catalyst TK-710. Symbol (○) represents the experimental results from Ref. [23]. The solid line is the modeling results using the simultaneous adsorption and reaction mechanism with first-order reaction. The dashed line is the modeling results using the poisoning mechanism with the first-order reaction and deactivation.

Table 1
Estimated parameter values of the proposed decaying mechanisms

Mechanism	n	Parameter	Catalyst	
			F-145	TK-710
Simultaneous adsorption and reaction	1	K (10^{-3} m^3/g-V)	9.26 ± 0.85	9.22 ± 0.59
		k_i (10^{-9} m/h)	4.42 ± 1.72	2.05 ± 0.64
		D_e (10^{-8} cm^2/s)	4.68 ± 3.36	5.34 ± 1.80
		Φ_{pn}	0.93	0.80
	2	K (10^{-3} m^3/g-V)	9.00 ± 0.63	8.80 ± 1.41
		k_i (10^{-11} m^4 g-V^{-1} h^{-1})	1.10 ± 0.17	0.44 ± 0.04
		D_e (10^{-8} cm^2/s)	4.79 ± 2.37	5.46 ± 2.67
		Φ_{pn}	1.14	0.98
Poisoning of metal deposition ($m = 1$)	1	k_i (10^{-9} m/h)	9.11 ± 2.67	5.18 ± 1.23
		k_d (10^{-3} m^3 g-V^{-1} h^{-1})	2.60 ± 1.56	1.60 ± 0.65
	2	k_i (10^{-11} m^4 g-V^{-1} h^{-1})	4.06 ± 1.81	1.80 ± 0.57
		k_d (10^{-3} m^3 g-V^{-1} h^{-1})	3.46 ± 2.15	1.94 ± 0.79

n, surface reaction order; m, deactivation order, K, adsorption equilibrium constant for the Langmuir isotherm; k_i, rate constant of the intrinsic reaction; D_e, effective diffusivity; Φ_{pn}, generalized Thiele modulus; k_d, rate constant of the intrinsic deactivation.

activity of the catalysts was followed by the apparent conversions of vanadium. It was not only because the vanadium concentration in the feed was much higher than that of nickel (510 ppm V and 66 ppm Ni), but also because the unevenly distributed tendency of the vanadium deposition mostly contributed to the catalyst decay [3]. Although there was some scattering in the data, two distinct periods in each of the runs were still recognized: an initial quickly declining period followed by a much longer period with steady activity.

The stabilized period indicated that the activity of the catalysts was not greatly affected by the carbonaceous and metal deposition after the beginning stage. Of course, it was not surprising for the catalysts that were designed to have a large average pore diameter and a high capacity of deposit uptake in order to pretreat residual oils. Thereby, in the modeling it was reasonably assumed that the effective diffusivity of the reactants inside the particle was not significantly changed within the limited running time. In addition, since the demetallization rate has been considered to be first order [9–11,13,14,16–20] and second order [1,12,15] in the metal concentration without general agreements, both of the reaction orders were examined for each of the mechanisms. Nevertheless, due to lack of information the empirical decay laws for the poisoning mechanism were checked only with the first- and the second-order deactivation. The monolayer coverage of vanadium deposition q_0^* has been calculated to be in the range of $1.7–8.8 \times 10^{-4}$ g V/m^2 of catalyst [1,25]. The exact value depended on crystallographic orientation of the deposit relative to the catalyst surface [1]. However, Pereira and Beeckman reported that the monolayer coverage for Boscan vacuum feed was about 4×10^{-4} g V/m^2 of catalyst [16], which was compatible with our experimental conditions. Therefore, this value that happened to be the median and has been used in several papers [16,19,20] was also chosen in this study. There were three adjustable parameters in the poisoning mechanism: effective diffusivity D_e, rate constant of the intrinsic reaction k_i, and rate constant of the intrinsic deactivation k_d. Because either k_i or D_e had to be fixed during the regression to avoid overparameterization, the values of D_e for the poisoning mechanism were adopted directly from the simultaneous adsorption and reaction mechanism in this work.

In result, it was found that the catalyst decaying obviously did not follow the second-order deactivation with the poisoning mechanism. Moreover, for either mechanism with the different reaction orders, the fit curves were identical but the parameter values were different. The detailed results of the modeling are given in Table 1 and Figs. 1 and 2, in which the first-order deactivation was employed throughout.

As shown in Table 1, the estimated effective diffusivity was centered at $5 \times 10^{-8}\ \mathrm{cm}^2/\mathrm{s}$ for both of the catalysts. This magnitude of D_e values was in good agreement with previous studies in which the effective diffusivity of metal-bearing compounds was reported to range between 10^{-8} and $10^{-7}\ \mathrm{cm}^2/\mathrm{s}$ [9,26–28]. A smaller value of D_e in our case was expected since the Venezuelan heavy vacuum residue was used. Having the values of k_i and D_e, a dimensionless term the generalized Thiele modulus Φ_pn that was an index of intraparticle mass-transfer limitation was calculated according to the definition:

$$\Phi_\mathrm{pn} = \frac{R}{g}\sqrt{\frac{\frac{n+1}{2} k_\mathrm{i} S_\mathrm{a} \rho_\mathrm{c} C_\mathrm{i}^{n-1}}{D_\mathrm{e}}}. \tag{10}$$

Consequently, the largest Φ_pn of the two catalysts in the stabilized period was 1.14, suggesting that the diffusional limitation was not serious even at the end of the runs. Thereby, the assumption that within the limited running time the effective diffusivity was not significantly changed by the further deposition was justified. The predictions from the two models in the examples of the first-order reaction kinetics are given in Figs. 1 and 2 as well. Although the data quality was not very high, it was apparent that the model with the simultaneous adsorption and reaction mechanism followed the trends of the observations much better than the model purely with the poisoning mechanism. The latter obviously did not distinguish the two distinct regions, which resulted from a compromise between the different decaying rates.

Notably, the calculated activity using the poisoning mechanism was going to be zero very quickly if the deactivation rate were maintained. This consequence would be in contradiction with the observations that there was always some residual activity left after the initial stage. Thereby, additional factors had to be included into the model to correct the predictions. In the literature, an autocatalytic mechanism that the metal deposits themselves created new active sites was mostly proposed. However, in our preceding study it was strongly doubted that the activity especially the hydrogenolysis activity or metal-removal activity deriving from the deposits could reach such a high level to compensate the activity loss of a commercial catalyst [21]. Furthermore, even if the autocatalytic effects were significant, a lot of concerned questions have still not been answered since they were put forward by Toulhoat et al. [18], implying that the theory was incomplete and unconvincing.

On the contrary, by interpreting the initial decay as an effect of decreasing adsorption on the alumina support rather than deactivation of the original active sites, the simultaneous adsorption and reaction mechanism explained the whole process simply and reasonably. Of great importance, the new model exhibited the same typical characters as the model with the corrected poisoning mechanism: the initial stage was related to the metal concentrations of the feed and the monolayer coverage capacity of the catalyst, and after the initial period there was a residual activity left. Therefore, it was concluded that the new mechanism was good and convincing enough to explain the initial decay of the HDM catalysts with real petroleum feeds.

It was known that a good understanding of the catalyst deactivation is essential for further development of long-life HDM catalysts. Thus, though still preliminary, we believe that the new mechanism would broaden our outlook and give new insight into the decay of the HDM catalysts at a commercial operation.

4. Conclusions

Without the correction of the autocatalytic hypothesis, the purely poisoning model of the metal deposition fits the aging experimental data of the two HDM catalysts very poorly. On the contrary, the model based on the simultaneous adsorption and reaction mechanism newly suggested in our preceding study follows the trends of the experimental observations much better. Instead of interpreting the initially decreasing activity as a result of catalyst deactivation, the new mechanism explains the process simply and reasonably: the initial apparent activity is an effect of a nearly constant catalytic activity of the active phase coupled with an extra decreasing adsorption on the alumina support. Moreover, the new model also possesses the representative characters of the one with the corrected poisoning mechanism: the initial stage is related to the metal concentrations of the feed and the monolayer coverage capacity of the catalyst, and after the initial period there is a residual activity left. Therefore, the simultaneous adsorption and reaction mechanism is good and convincing enough to explain the initial decay of the HDM catalysts with real petroleum feeds.

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