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A Model for the Aging of Redox Catalysts[1]

TEH CHUNG HO

Corporate Research Laboratories, Exxon Research and Engineering Co., Linden, New Jersey 07036

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A mathematical model is presented to describe the aging of the Mars–van Krevelen redox catalysts in a situation of practical interest. It is shown that the aging kinetic parameters can be obtained from a minimum amount of initial life data. A theoretical upper limit on catalyst lifetime is derived in terms of the kinetic and operation parameters, which for practical purposes can be used as an a priori estimate of catalyst lifetime. Also, the model suggests means of extending catalyst life. Finally, model predictions are shown to compare favorably with published data. It is hoped that the model will serve as a tool for data correlation as well as for prediction of catalyst service life from short-term experiments such as accelerated aging.

INTRODUCTION

The kinetic treatment of the redox cycle mechanism for hydrocarbon selective oxidations on metal oxides appears to date from the work of Mars and van Krevelen in 1954 (*1*). In this mechanism, the reactant hydrocarbon is oxidized with the lattice oxygen on sites of high oxidation state to yield the reaction product and simultaneously those sites are reduced to a lower oxidation state. The resulting lower oxidation state sites are then reoxidized with the reactant oxygen to replenish the consumed higher oxidation state sites. These two steps can be repeated indefinitely under proper conditions. Based on this mechanism, Mars and van Krevelen deduced the kinetics of this redox cycle as follows:

Let θ_H and θ_L be the fractions of active phases in high and low oxidation states, respectively, then it is assumed that the rates of reduction r_{red} and reoxidation r_{reox} are of the form

$$r_{red} = K_1 C^m \theta_H \tag{1}$$

$$r_{reox} = K_2 C_O{}^n \theta_L \tag{2}$$

where C and C_O are concentrations of hydrocarbon and oxygen, respectively, and K_1 and K_2 are Arrhenius type rate constants, i.e.,

$$K_1 = A_1 e^{-E_1/RT} \tag{3}$$

$$K_2 = A_2 e^{-E_2/RT}. \tag{4}$$

Suppose further that a is the number of oxygen molecules required to oxidize one molecule of hydrocarbon, then at steady state ($r_{reox} = ar_{red}$) and with no deactivation ($\theta_H + \theta_L = 1$ at all times) we have

$$\theta_H = \frac{K_2 C_O{}^n}{aK_1 C^m + K_2 C_O{}^n} \tag{5}$$

Substituting Eq. (5) into Eq. (1), the rate of hydrocarbon oxidation r takes the form

$$r = \frac{K_1 C^m}{1 + \dfrac{aK_1 C^m}{K_2 C_O{}^n}}. \tag{6}$$

Data obtained from kinetic (both transient and steady state) and isotope labeling experiments have demonstrated that the above mechanism and kinetics indeed prevail in a variety of hydrocarbon selective oxidations on metal oxide catalysts (*2–5*).

This study was motivated by the observation that commercial metal oxide catalysts

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often become totally deactivated with continued use over periods of years. Life studies of such catalyst systems not only are expensive but have remained a totally empirical art. Accordingly, there is a need for a mathematical model which can serve as a guide for data correlation and when combined with suitable short-term experiments, such as accelerated aging, may predict the service life of the catalyst. In view of this, the purposes of the present study are (1) to introduce a catalyst aging model for the Mars–van Krevelen redox catalysts, and (2) to illustrate the use of the model by analyzing the aging behavior of a redox catalyst in a fixed-bed plug-flow reactor operated at a constant exit conversion through temperature adjustment. Such a constant-conversion-rising-temperature practice is quite common in commercial oxidation processes.

THE MODEL

Catalyst deactivation experienced in petroleum processes is mostly caused by the deposition of foreign materials (e.g., coke or metals). This mechanism at best is of secondary importance in selective oxidation reactions. A Mars–van Krevelen redox catalyst may lose its activity because during the redox cycle either the low oxidation state phase θ_L or the high oxidation state phase θ_H may be converted slowly to a catalytically inactive phase θ_I through deeper reduction, structure change, or volatilization of a particular catalyst constituent. (This deactivation process is often accompanied by a color change.) Without loss of generality, in the following development we consider only the case in which the θ_L phase becomes converted irreversibly to the inactive θ_I phase. Schematically, this can be represented by Fig. 1. For simplicity the rate of deactivation r_D is assumed to be

$$r_D = K_3 C\theta_L = A_3 e^{-E_3/RT} C\theta_L. \quad (7)$$

We note that for most situations of practical interest $K_3 \ll K_1$, K_2 and $E_3 > E_1$, E_2.

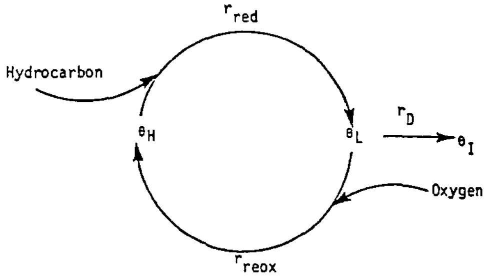

FIG. 1. Aging model for the Mars–van Krevelen redox catalyst.

CATALYST LIFE AT CONSTANT CONVERSION

To illustrate the use of the above model, we consider a fixed-bed plug-flow catalytic reactor at temperature T with a linear velocity V and a holding time on the order of K_1^{-1}. The concentration of oxygen in the reactor can be expressed in terms of that of hydrocarbon, i.e., $C_O = pC_f - a(C_f - C)$ where p is the oxygen-to-hydrocarbon ratio in the feed and C_f the inlet concentration of hydrocarbon. A mass balance for C, θ_H, and θ_L at any point z, $0 \le z \le l$, of the reactor and at an instant t can be written as

$$\frac{\partial C}{\partial t} + V\frac{\partial C}{\partial z} = -K_{1S}C^m\theta_H e^{-[E_1/R(1/T - 1/T_S)]} \quad (8)$$

$$\omega(1-\varepsilon)\rho_c\frac{\partial \theta_H}{\partial t} = -aK_{1S}C^m\theta_H e^{-[E_1/R(1/T-1/T_S)]} + K_{2S}(b+aC)^n\theta_L e^{-[E_2/R(1/T-1/T_S)]} \quad (9)$$

$$\omega(1-\varepsilon)\rho_c\frac{\partial \theta_L}{\partial t} = -K_{2S}(b+aC)^n\theta_L e^{-[E_2/R(1/T-1/T_S)]} + aK_{1S}C^m\theta_H e^{-[E_1/R(1/T-1/T_S)]} - K_{3S}C\theta_L e^{-[E_3/R(1/T-1/T_S)]} \quad (10)$$

where T_S is the start-of-run temperature, ε the reactor void fraction, ρ_c the catalyst apparent density, ω the weight fraction of active materials in the catalyst, $b \equiv (p - a)C_f$, and

$$K_{iS} = A_i e^{-E_i/RT_S} \qquad i = 1, 2, 3. \quad (11)$$

Accordingly, the catalyst activity at any instant of time within the reactor is given by the solution of the above equations. However, finding the solution is less appealing in terms of return on effort expended because our primary concern is the long-term behavior of the catalyst. So instead in the analysis to follow we seek an asymptotic solution for large times. This is based on the following physical reasoning: Since the activity decline under consideration can only be measured in a time frame characterized by K_{3S}^{-1}, which is significantly larger than the time scales of the redox reaction and flow, it can be visualized that θ_H and θ_L would quickly reach a steady state dictated by the Mars–van Krevelen kinetics at the start of a life experiment. Subsequently, θ_H and θ_L, while preserving the redox cyclic structure, will diminish concurrently as time passes. In other words, the reactor is operating at a quasi-steady state ($K_{3S}/K_{1S} \ll 1$) and consequently Eqs. (8) through (10) for large times can be asymptotically reduced to

$$V\frac{\partial C}{\partial z} = -K_{1S}C^m\theta_H e^{\gamma_1\phi/(1+\phi)} \quad (12)$$

$$aK_{1S}C^m\theta_H e^{\gamma_1\phi/(1+\phi)} = K_{2S}(b + aC)^n\theta_L e^{\gamma_2\phi/(1+\phi)} \quad (13)$$

$$\omega(1 - \varepsilon)\rho_c \frac{\partial}{\partial t}(\theta_H + \theta_L) = -K_{3S}C\theta_L e^{\gamma_3\phi/(1+\phi)} \quad (14)$$

where $\gamma_i \equiv E_i/RT_S$ with $i = 1, 2, 3$ and ϕ is a dimensionless temperature defined as

$$\phi \equiv \frac{T}{T_S} - 1. \quad (15)$$

It is clear that using the above quasi-steady-state approximation, we are able to simplify the original equations by decoupling the redox and aging processes.

As pointed out earlier, it is of practical interest to inquire about the life behavior of an aging catalyst operated at a constant exit conversion by raising temperature. It follows from Eq. (12) that the conversion of hydrocarbon at the reactor exit can be made independent of onstream time if the reactor temperature is raised continuously to satisfy

$$\frac{\partial}{\partial t}[\theta_H e^{\gamma_1\phi/(1+\phi)}] = 0. \quad (16)$$

That is to say

$$\theta_H e^{\gamma_1\phi/(1+\phi)} = \theta_H(0). \quad (17)$$

To complete the problem statement, we need to specify the "initial" condition—that is, the state of the catalyst at the start of a life experiment. In light of the preceding reasoning, it is appropriate to assign the following initial conditions:

$$t = 0 \qquad \theta_H = \frac{1}{1 + \sigma} \quad (18)$$

$$\theta_L = \frac{\sigma}{1 + \sigma} \quad (19)$$

where σ is a redox parameter defined as

$$\sigma \equiv \frac{aK_{1S}C_S^m}{K_{2S}(b + aC_S)^n} \quad (20)$$

with C_S being the concentration of hydrocarbon at the reactor exit. Combining Eqs. (17) and (18) gives the relation between reactor temperature and catalyst activity

$$e^{\phi/(1+\phi)} = \left[\frac{1}{(1 + \sigma)\theta_H}\right]^{1/\gamma_1}. \quad (21)$$

Substituting Eq. (21) into Eq. (13) yields

$$\theta_L = \sigma(1 + \sigma)^{\lambda - 1}\theta_H^{\lambda} \quad (22)$$

where

$$\lambda \equiv \frac{\gamma_2}{\gamma_1} \quad (23)$$

which means that in constant-conversion operation θ_L diminishes as θ_H raised to the λ power in order to maintain the redox cycle at a quasi-steady state. Further, substituting Eq. (21) into Eq. (14) leads to

$$\frac{\partial\theta_L}{\partial t} = -\frac{\partial\theta_H}{\partial t} - \frac{\alpha K_{3S}}{(1 + \sigma)^{\mu}}\theta_H^{-\mu}\theta_L \quad (24)$$

where

$$\mu \equiv \frac{\gamma_3}{\gamma_1} > 1 \tag{25}$$

$$\alpha \equiv \frac{C_S}{\omega(1-\varepsilon)\rho_c}. \tag{26}$$

Using Eq. (22), one can decouple Eq. (24) to yield an equation for θ_H only, namely

$$[1 + \lambda\sigma(1+\sigma)^{\lambda-1}\theta_H{}^{\lambda-1}]\frac{\partial\theta_H}{\partial t} = -\alpha K_{3S}\sigma(1+\sigma)^{\lambda-\mu-1}\theta_H{}^{\lambda-\mu}. \tag{27}$$

With Eq. (18) as the initial condition, Eq. (27) is readily integrated to give a closed-form expression for θ_H as an implicit function of onstream time, that is

$$\alpha K_{3S}t = \frac{\lambda}{\mu}\{1 - [(1+\sigma)\theta_H]^{\mu}\} + \frac{1}{\sigma(\mu-\lambda+1)}\{1 - [(1+\sigma)\theta_H]^{\mu-\lambda+1}\}. \tag{28}$$

Since the temperature ϕ is readily measureable, it is convenient to express the temperature as a function of onstream time. To this end substituting Eq. (21) into Eq. (28), we obtain

$$\alpha K_{3S}t = \frac{\lambda}{\mu}\{1 - \exp[-\gamma_1\mu\phi/(1+\phi)]\} + \frac{1}{\sigma(\mu-\lambda+1)}\{1 - \exp[-\gamma_1(\mu - \lambda + 1)\phi/(1+\phi)]\}. \tag{29}$$

Since in practice the constant-conversion run ends at the maximum operable temperature $T_{\max}$, usually the temperature at which the target conversion can no longer be obtained, we may define catalyst lifetime L as the time span between the start and the end of the run. From Eq. (29) L can be readily calculated by

$$L = \frac{\lambda}{K_{3S}\mu\alpha}\{1 - \exp[-\gamma_1\mu\phi_m/(1+\phi_m)]\} + \frac{1}{K_{3S}\sigma(\mu-\lambda+1)\alpha}\{1 - \exp[-\gamma_1(\mu - \lambda + 1)\phi_m/(1+\phi_m)]\} \tag{30}$$

where

$$\phi_m \equiv \frac{T_{\max}}{T_S} - 1. \tag{31}$$

PARAMETER ESTIMATION FROM INITIAL LIFE DATA

Equation (29) can be used for the simultaneous determination of the aging kinetic parameters K_{3S} and μ from a single constant-conversion life experiment by matching the predicted and observed temperature rise profiles. This procedure, however, could be time consuming and costly even if the life experiment is conducted at the accelerated conditions. [A general discussion on accelerated aging can be found in (*6*).] A problem of practical interest is therefore the estimation of the aging kinetic parameters from a minimum amount of initial life data. In what follows we outline such a procedure based on the present model.

Expanding the right-hand side of Eq. (28) around the initial condition $(1+\sigma)\theta_H = 1$ and keeping only the first-order term, we obtain for small t an equation free of μ

$$\frac{1}{\alpha}\left(\lambda + \frac{1}{\sigma}\right)[1 - (1+\sigma)\theta_H] = K_{3S}t. \tag{32}$$

Substituting Eq. (21) into Eq. (32) gives

$$\frac{1}{\alpha}\left(\lambda + \frac{1}{\sigma}\right)[1 - e^{-\gamma_1\phi/(1+\phi)}] = K_{3S}t \tag{33}$$

so a plot of the left-hand side vs onstream time will be linear with slope K_{3S}. Analogous to the conventional method of kinetic analysis, here the activation energy μ can be determined from several constant-conversion experiments with different T_S's.

In cases where $\gamma_1\phi$ is small (say $< 10^{-2}$), Eq. (33) can be further simplified and rearranged to

$$\frac{T_S}{T} \approx 1 - \frac{\alpha K_{3S}}{\gamma_1\left(\lambda + \frac{1}{\sigma}\right)}t. \tag{34}$$

The above equation has the same structure as that developed (*6*) for a different deactivating catalyst system in that a linear plot of $1/T$ vs t gives the value of K_{3S}. The added feature here is the inclusion of λ and σ to account for the redox nature of the catalyst.

UPPER BOUND ON CATALYST LIFE

In catalyst exploratory work, sometimes a priori knowledge of $T_{\max}$ is not available. Under such circumstances, it is often desirable to have an upper bound on catalyst life in terms of the kinetic and operation parameters. To this end, we see from Eq. (21) that

$$\phi \to \infty \text{ as } \theta_H \to \frac{e^{-\gamma_1}}{1+\sigma} \tag{35}$$

that is, unrealistically large temperatures are required to maintain constant conversion when θ_H diminishes to the limiting value $e^{-\gamma_1}/(1+\sigma)$. Setting $\theta_H = e^{-\gamma_1}/(1+\sigma)$ in Eq. (28), we obtain an upper bound U for catalyst lifetime

$$L < U \tag{36}$$

where

$$U \equiv \frac{1}{K_{3S}\alpha}\left\{\frac{\lambda}{\mu}\left[1 - e^{-\gamma_1\mu}\right] + \frac{1}{\sigma(\mu - \lambda + 1)}\left[1 - e^{-\gamma_1(\mu-\lambda+1)}\right]\right\}. \tag{37}$$

Usually, the two exponential terms in the above equation are negligibly small, so for practical purposes U can be calculated by

$$U \approx \frac{1}{K_{3S}\alpha}\left[\frac{\lambda}{\mu} + \frac{1}{\sigma(\mu - \lambda + 1)}\right]. \tag{38}$$

Equation (38) indicates that catalyst lifetime depends primarily on the ratios of activation energies rather than their magnitude. Further, since K_{3S} is more sensitive to temperature than α, T_S should be chosen as low as permissible in order to extend the life of the catalyst. Moreover, to prolong catalyst life we need to design a catalyst having a high reoxidation ability (i.e., $K_{2S} > K_{1S}$) and/or operate the catalyst at the highest permissible oxygen-to-hydrocarbon ratio, say near the edge of the flammable region.

COMPARISON WITH EXPERIMENT

In Fig. 2 are shown the life data obtained from an accelerated aging experiment on the oxidation of methacrolein to methacrylic acid at 80% conversion over a multicomponent catalyst (*7*). The redox phenomenon of this reaction system has recently been discussed by Misono (*8*) and Konishi *et al.* (*9*).

It should be reemphasized that the whole of the foregoing analysis is based on the observation that the aging time scale is much larger than the characteristic time scale of the redox cycle (quasi-steady-state approximation). A corollary of this is to state that the parameters α, λ, σ, and γ_1—for practical purposes—may be determined

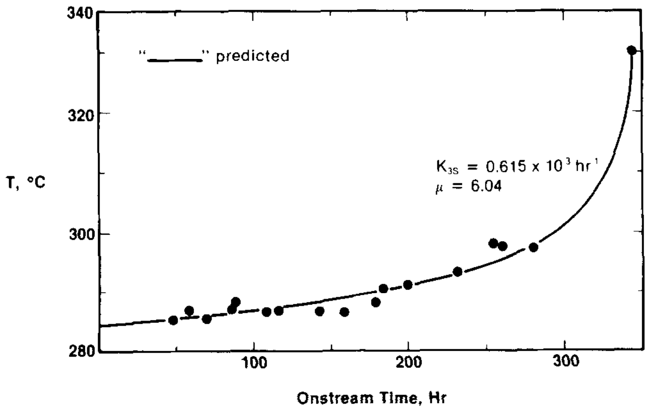

FIG. 2. Comparison of model prediction and experimental data.

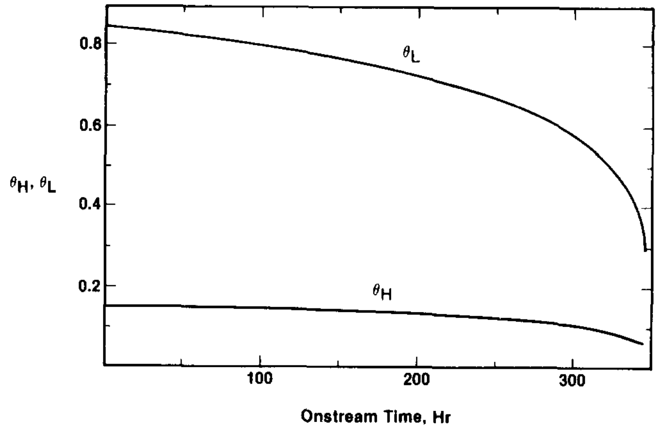

FIG. 3. Depletion history of the redox couple θ_H and θ_L.

from experiments essentially free of catalyst deactivation. The data in Fig. 2 can then be used for estimating the only two adjustable parameters in the model, K_{3S} and μ. To estimate them by a least-squares fit of Eq. (29) to the data, we took $\alpha = 1.0$, $\lambda = 1.1$, $\sigma = 5.5$, and $\gamma_1 = 11.42$. In addition, we read from Fig. 2 that $T_S = 284°C$ and $T_{max} = 330°C$.

Before proceeding further, some words about the least-squares fit are perhaps in order. Since Eq. (29) is explicit with respect to onstream time t, the deactivation parameters may be estimated by choosing them to minimize the following objective function J based on time, i.e.,

$$J = \sum_{j=1}^{N} (t_j - \hat{t}_j)^2 = \text{minimum} \qquad (39)$$

where $\hat{t}_j$ and t_j are the observed and calculated onstream times, respectively, and N is the total number of measurements. This procedure, while computationally simple, may give biased parameter values because time is not the true dependent variable. A statistically more meaningful procedure would be to base the objective function on temperature ϕ, that is, the parameters K_{3S} and μ are estimated by minimizing the following objective function Q

$$Q = \sum_{j=1}^{N} (\phi_j - \hat{\phi}_j)^2 = \text{minimum}. \qquad (40)$$

Clearly, in minimizing Q one has to solve Eq. (29) numerically to obtain ϕ for a given t. Of course, when the data are of high accuracy, both procedures would give results in close agreement.

In light of the above discussion, Eq. (40) was used to estimate K_{3S} and μ. The best set of parameter values so found was

$$K_{3S} = 0.615 \times 10^{-3}\ \text{hr}^{-1}$$

$$\mu = 6.04.$$

These values were then used to generate the predicted temperature rise shown as the solid curve in Fig. 2. As seen, the agreement between the theory and experiment is satisfactory considering the scatter of the data. Using Eq. (38), the catalyst lifetime under the accelerated conditions was estimated to be 346 hr, compared with 344 hr observed experimentally. If desired, the deactivation parameters determined from the above accelerated aging data can be used to predict the life of the catalyst under normal operating conditions.

Of course, in catalyst life studies it is most desirable to be able to determine the deactivation kinetic parameters from the initial life data obtained from accelerated aging. For example, we may estimate K_{3S} from Eq. (34) using the datum at hour 48 in Fig. 2. This yields a K_{3S} value of $0.547 \times 10^{-3}\ \text{hr}^{-1}$, which gives an estimated catalyst life of 389 hr—still in reasonably good agreement with the experimental value of 344 hr.

Finally, the shape of the temperature rise deserves some comments. The predicted temperature rise in Fig. 2 is characterized by a long slow deactivation period followed by a rapid acceleration of the deactivation. Note further that the deactivation over the long "induction" period (~150 hr) is so mild that the temperature increase over this period is within the experimental scatter. Physically, this induction period may be interpreted as arising from the nucleation of the inactive θ_I phase. And the subsequent rapid deactivation may result from the growth of that phase. Figure 3 shows the predicted depletion of the redox couple; it is seen that the depletion occurs rapidly toward the end of catalyst life.

CONCLUDING REMARKS

A model has been developed to consider the fact that the Mars–van Krevelen redox catalysts often deactivate slowly during use. This is done by incorporating within the Mars–van Krevelen redox framework an aging mechanism. The aging process is described quantitatively using a quasi-steady-state approximation. A simple experimental procedure is outlined for the determination of the aging parameters from initial life data. Also, a theoretical upper bound for catalyst lifetime is derived in terms of the kinetic and operation parameters. The model in addition suggests means of extending catalyst life. A comparison of the model predictions and published data suggests that the model may serve as a correlative as well as a predictive tool.

Although in the present study it is assumed that the deactivation follows a first-order kinetics, modification of the present analysis to accommodate any deactivation kinetics (e.g., $r_D = K_3 C \theta_L{}^d$) of practical interest is straightforward.

NOTATION

A_1	Pre-exponential factor for reduction reaction
A_2	Pre-exponential factor for reoxidation reaction
A_3	Pre-exponential factor for deactivation
a	Stoichiometric coefficient
b	Defined as $(p - a)C_f$
C	Concentration of hydrocarbon
C_O	Concentration of oxygen
C_f	Inlet concentration of hydrocarbon
C_S	Exit concentration of hydrocarbon
d	Deactivation order
E_1	Activation energy for reduction reaction
E_2	Activation energy for reoxidation reaction
E_3	Activation energy for deactivation
J	Objective function defined by Eq. (39)
K_1	Rate constant for reduction reaction
K_2	Rate constant for reoxidation reaction
K_3	Rate constant for deactivation
K_{iS}	Rate constants evaluated at T_S ($i = 1, 2, 3$)
l	Length of reactor
L	Catalyst lifetime
m	Reaction order defined in Eq. (1)
n	Reaction order defined in Eq. (2)
N	Total number of measurements
p	Ratio of oxygen to hydrocarbon in the feed
Q	Objective function defined by Eq. (40)
R	Gas constant
r_{red}	Rate of reduction
r_{reox}	Rate of reoxidation
r_D	Rate of deactivation
T	Reactor temperature
T_{max}	Maximum allowable temperature
T_S	Start-of-run temperature
t	Time-on-stream
$\hat{t}$	Observed onstream time
U	Upper bound for catalyst lifetime
V	Linear velocity
z	Length coordinate in the reactor

Greek Symbols

α	Defined as $C_S/[\omega(1 - \varepsilon)\rho_c]$
γ_i	Defined as E_i/RT_S ($i = 1, 2, 3$)

θ_H	Fraction of high oxidation state phase
θ_L	Fraction of low oxidation state phase
θ_I	Fraction of inactive phase
λ	Defined as E_2/E_1
σ	Defined in Eq. (20)
μ	Defined as E_3/E_1
ϕ	Dimensionless temperature defined as $(T/T_S) - 1$
$\hat{\phi}$	Observed dimensionless temperature
ϕ_m	Dimensionless maximum temperature defined as $(T_{max}/T_S) - 1$
ρ_c	Catalyst apparent density
ε	Reactor void fraction
ω	Weight fraction of active materials in the catalyst

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