

# Kinetic Study on Air Regeneration of Industrial Methanol-to-Olefin Catalyst

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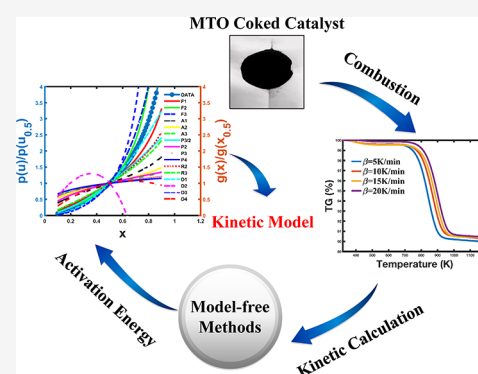
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**ABSTRACT:** The regeneration kinetics of coke on an industrial methanol-to-olefin (MTO) catalyst was studied via thermogravimetric analysis under the air atmosphere. To minimize the uncertainty of the kinetic parameters, four model-free methods were employed to calculate the regeneration activation energy. It was found that the activation energies obtained by all methods are quite consistent for any given coke conversion. An average activation energy of 141.1 kJ/mol was obtained for combustion of coke on the industrial MTO catalyst. The master-plot method was then employed to decide the regeneration model function. It showed that the combustion process of coke on the industrial MTO catalyst may be depicted using the Fn model. A comparison between the model prediction and additional experimental results demonstrated that the regeneration kinetics model built in this work can work very well under operation conditions of industrial interest and favor the optimization and design of a regenerator in an industrial MTO unit.



## 1. INTRODUCTION

The methanol-to-olefin (MTO) reaction has gained great attention because it offers a possibility to produce basic chemicals from nonoil raw materials.<sup>1,2</sup> The SAPO-34 zeolite that manifests a high selectivity to light olefin is reported to be the most effective catalysts.<sup>1–3</sup> However, it suffers a quick deactivation because of coke deposition.<sup>1,4,5</sup> Therefore, recovery of the activity of catalysts, that is, catalyst regeneration, is crucial for industrial operation. Regeneration is often carried out via combustion of the coked catalyst in the air or oxygen-rich atmosphere.<sup>4,6</sup> Actually, in industrial MTO processes, a circulating fluidized bed is used to ensure continuous circulation of the catalyst.<sup>1</sup> Despite a large quantity of research carried out on the MTO reaction process, the combustion kinetics of the coked catalyst in the MTO regeneration process, however, has received little attention. Therefore, the establishment of a reliable and accurate regeneration kinetics model for the spent MTO catalyst is of practical importance in designing and optimizing an industrial MTO regenerator.

A thermogravimetric analyzer is frequently applied to decide the kinetic parameters of regeneration of coked catalysts,<sup>7–9</sup> pyrolysis of biomass,<sup>10</sup> and gasification of coal<sup>11</sup> and other solid raw materials. So far, there are many methods developed for evaluating kinetic parameters according to the data acquired using a thermogravimetric analyzer (TGA). These ways in general are classified into two kinds: model-fitting and model-free methods.<sup>12–14</sup> The popularity of the model-fitting method is that it can achieve a kinetic triplet at a single heating rate.<sup>12</sup> In this method, the kinetic parameters are usually

calculated via fitting the experimental data from a constant heating rate to numerous model functions.<sup>12</sup> Although many different model functions can fit the experimental values well, there is a significant difference in the achieved kinetic parameters.<sup>12,15</sup> In other words, these parameters obtained from the model-fitting method are largely dependent upon the model function chosen. Moreover, a single activation energy for the overall reaction process can only be obtained, so it is unable to reveal the complexity in, for instance, the solid-state reactions.<sup>15</sup> Conversely, the model-free method does not require any prior forms of model functions, avoiding possible errors associated with the choice of kinetic models.<sup>12,14</sup> In addition, it is capable of gaining the activation energy at different conversions of the reactant.<sup>12,14</sup> In these regards, the model-free method is superior to the model-fitting method.

Numerous works have been carried out to study combustion kinetics of the coked catalyst, such as fluid catalytic cracking catalysts,<sup>9,16,17</sup> catalytic reforming catalysts,<sup>18</sup> and so forth. Weisz and Goodwin reported that the coke combustion activation energy was about 160 kJ/mol for a silica-alumina cracking catalyst.<sup>17</sup> With the application of a zeolite catalyst in fluid catalytic cracking, the combustion of coke deposited on

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the zeolite, for example, the Y-type zeolite, has begun to attract attention. Dimitriadis et al. reported that the combustion activation energy for fluid catalytic cracking (FCC) zeolite catalysts was 157 kJ/mol.<sup>19</sup> Hano et al. investigated the regeneration of the deactivated Y kind zeolite and found that its activation energy is 110 kJ/mol. It was smaller than those reported in other works.<sup>20</sup> A comparative study about combustion rates of different kinds of coked zeolites was carried out by Magnoux and Guisnet.<sup>21</sup> They found the oxidation rates of coked HZSM-5 were lower than those of other zeolites. They attributed the difference to limited contact between oxygen and coke rather than the composition and location of the coke. Thus, they considered coke combustion is related to the zeolite structure. Li and Brown studied the regeneration kinetics of a cracker catalyst obtained at different coked temperatures. A five-step reaction model was put forward and the activation energy for formation of CO<sub>2</sub> was between 120 and 160 kJ/mol.<sup>22</sup>

In addition, numerous studies about regeneration kinetics of deactivated HZSM-5 zeolite catalysts have been carried out. Aguayo et al. found that the activation energy was 105 kJ/mol and the coke combustion rate was lower than those in other catalysts when they studied the combustion of the coked HZSM-5 zeolite in methanol to gasoline conversion.<sup>23</sup> To make out the coke combustion behavior was caused by the coke properties or the pore structure of the zeolite, Ortega et al. further compared the oxidation of the coke released from the HZSM-5 zeolite with that within the HZSM-5.<sup>24</sup> Results showed the oxidation rate of coke within the zeolite was lower than that released from the zeolite, which means that the combustion of coke is restricted by the porous structure of HZSM-5. Zhu et al. studied the regeneration behavior of the H-ZSM-5 catalyst.<sup>7</sup> They claimed that coke could be classified into two types, light coke and heavy coke, which were determined by feed composition. The combustion activation energy for light and heavy coke was 112 and 142 kJ/mol, respectively. Aguayo et al. also investigated the combustion of coked HZSM-5, which was for the conversion of aqueous ethanol to hydrocarbons.<sup>25</sup> The activation energy achieved was 123 kJ/mol, which was a little higher than that obtained in the process of methanol to gasoline conversion. They explained that there was a difference in H/C of coke. Jiang et al. applied TGA to study the regeneration kinetics of HZSM-5 in the methanol to propylene conversion process,<sup>26</sup> and they found an activation energy of 126.9 kJ/mol.

In industrial units, there is a stripping process usually for the coked catalyst for removing the volatile material before regeneration.<sup>27</sup> Therefore, in addition to focusing on the effect of the catalyst type and coking conditions, some attempts have been made to investigate the effect of aging treatment on catalyst regeneration combustion. Magnoux et al. reported that N<sub>2</sub>-aging treatment could cause a slight decrease in the coke content but heavy cyclization aromaticity.<sup>27</sup> Aguayo et al. used He, H<sub>2</sub>, and steam to treat the coked HZSM-5 catalyst, they found that the aging treatment had a significant effect on the ratio of hydrogen to carbon of coke. As a consequence, the combustion kinetic parameter will be different.<sup>28</sup>

From the abovementioned, it is clear that coke nature not only depends on the types of catalysts, but also the coking conditions (temperature, time, feed, and aging). Although some investigations have been performed to study regeneration kinetics of coked catalysts, there are only a few studies about the combustion kinetics of coke on industrial MTO catalysts.

Aguayo et al. studied regeneration kinetics for a laboratory-synthesized catalyst coked in the MTO reaction at a temperature lower than that in industrial MTO operation.<sup>6</sup> Their experiments only dealt with the experimental data for the single-heating rate via model-fitting method assuming a first-order reaction,<sup>6</sup> which may cause large uncertainty because of the complicated interplay between temperature, catalyst properties, and operational conditions in the MTO process. Moreover, the coke composition on the MTO catalyst is complicated.<sup>4,29</sup> Thus, the coke combustion process may include different reaction steps that is, parallel and series reactions.<sup>9,30</sup> Besides, it has been widely reported that the nature of coke evolves during the combustion process, which is evident from the change of the ratio of H/C.<sup>24,31</sup> Therefore, it is necessary to further study the combustion of coke on industrial MTO catalysts in-depth to obtain the kinetic parameters for use in industrial processes. Previous studies usually used model fitting, using which only single-kinetic parameters can be obtained for the whole coke combustion process, without considering the evolution of coke. In this work, we will employ an advanced method, the model-free method, to investigate the regeneration of the industrial MTO catalyst. The model-free methods can be used to obtain kinetic parameters at different conversions of coke during the combustion process and minimize the model uncertainties associated with the choice of model function. Furthermore, we will apply the master-plot method, rather than the first-order model, to determine an appropriate reaction model for describing the coke combustion.

The objective of this work is to study the regeneration kinetics of the industrial MTO catalyst using model-free methods. To minimize the uncertainty of kinetics, TGA of combustion of coke on the MTO catalyst was carried out at numerous heating rates in the air atmosphere. Three most common integral forms of model-free approaches, that is, FWO and KAS as well as the Vyazovkin approach, and a differential form, that is, the Friedman approach, were utilized to decide the value of activation energy (*E*). Based on the obtained value of *E*, the master-plot method is further utilized to derive the regeneration model function.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of the Coked Catalyst Sample.** In this study, an industrial MTO catalyst (Chia Tai Energy Material) was employed for the regeneration kinetics study. Detailed physical parameters of the catalyst were described in our previous literature.<sup>1</sup> The MTO reaction was conducted in a laboratory scale fluidized bed reactor. Its inner diameter and height was 26 and 350 mm, respectively. A detailed diagram of the experimental facility could be found in our previous work.<sup>32</sup> Before every run, the template agent in the fresh catalyst was taken away via calcination at 923 K in air for 6.0 h. The coked catalyst samples were obtained from the following MTO reaction conditions (coking conditions): reaction temperature, 748 K; reaction pressure, atmospheric pressure; weight hour space velocity: 2.1 h<sup>-1</sup>; and reaction time: 2.0 h.

**2.2. Nonisothermal TGA Combustion Tests.** The combustion of the coked catalyst was performed using a TGA-SDT Q600 from TA Instruments. The instrument is capable of directly measuring and recording the weight loss of the coked catalyst during the reaction. The crucible used is made of Al<sub>2</sub>O<sub>3</sub> and its diameter and height are 6 and 4 mm, respectively. A thermocouple was located below the crucible,

Table 1. Model Functions Used for MTO Catalyst Regeneration

model	symbol	$f(x)$	$g(x)$
<b>Reaction-Order Model<sup>34</sup></b>			
first order	F1	$1 - x$	$-\ln(1 - x)$
second order	F2	$(1 - x)^2$	$(1 - x)^{-1} - 1$
three order	F3	$(1 - x)^3$	$[(1 - x)^{-2} - 1]/2$
<b>Nucleation Model<sup>34</sup></b>			
Avrami–Erofeev	A2	$2(1 - x)[- \ln(1 - x)]^{1/2}$	$[- \ln(1 - x)]^{1/2}$
Avrami–Erofeev	A3	$3(1 - x)[- \ln(1 - x)]^{2/3}$	$[- \ln(1 - x)]^{1/3}$
Avrami–Erofeev	A4	$4(1 - x)[- \ln(1 - x)]^{3/4}$	$[- \ln(1 - x)]^{1/4}$
<b>Diffusion Model<sup>34</sup></b>			
one-dimensional	D1	$1/2x$	$x^2$
two-dimensional	D2	$[- \ln(1 - x)]^{-1}$	$(1 - x)\ln(1 - x) + x$
three-dimensional	D3	$(3/2)(1 - x)^{2/3}[1 - (1 - x)^{1/3}]^{-1}$	$[1 - (1 - x)^{1/3}]^2$
three-dimensional	D4	$(3/2)[(1 - x)^{-1/3} - 1]^{-1}$	$(1 - 2x/3) - (1 - x)^{2/3}$
<b>Geometrical Contraction<sup>34</sup></b>			
contracting area	R2	$2(1 - x)^{1/2}$	$[1 - (1 - x)^{1/2}]$
contracting volume	R3	$3(1 - x)^{2/3}$	$[1 - (1 - x)^{1/3}]$
<b>Exponential Nucleation<sup>9</sup></b>			
power law	P4	$4x^{3/4}$	$x^{1/4}$
power law	P3	$3x^{2/3}$	$x^{1/3}$
power law	P2	$2x^{1/2}$	$x^{1/2}$
power law	P2/3	$2/3x^{-1/2}$	$x^{3/2}$

Table 2. Four Methods Used for Calculating Regeneration Activation Energy

method	model formula
FWO <sup>14,36</sup>	$\ln \beta_i = \ln[Ah(P_{O_2})E_x/Rg(x)] - 5.331 - 1.052E_x/RT_x$ (6)
KAS <sup>14,37</sup>	$\ln(\beta_i/T_x^2) = \ln[Ah(P_{O_2})E_x/Rg(x)] - E_x/RT_x$ (7)
Vyazovkin <sup>14,38</sup>	$\sum_{i=1}^n \sum_{j \neq i}^n [I(E_x, T_{x,i})\beta_i]/[I(E_x, T_{x,j})\beta_j] = \min$ (8)
Friedman <sup>14,39</sup>	$\ln[\beta_i dx/dT_x] = \ln[Af(x)h(P_{O_2})] - E_x/RT_x$ (9)

which is used to measure temperature. In every run, about 15 mg coked catalyst was kept in the alumina crucible and heated from room temperature to 1173 K in the air atmosphere at 5, 10, 15, and 20 K/min, respectively. The thickness of the catalyst sample in the crucible was roughly 1 mm. The air flow rate was kept at 100 mL/min. All experiments were performed three times to guarantee the data repeatability. Before the study, different air flow rate and catalyst mass tests were conducted to diminish the influence of mass transfer and heat transfer. In addition, the Weisz–Prater criterion was adopted to evaluate the impact of the infernal diffusion.<sup>33</sup>

### 3. KINETIC THEORY

The regeneration of the coked MTO catalyst is a typical gas–solid reaction. Therefore, the regeneration equation is expressed as<sup>14</sup>

$$dx/dt = k(T)f(x)h(P_{O_2}) = A \exp(-E/RT)f(x)h(P_{O_2}) \quad (1)$$

where  $dx/dt$  represents the catalyst regeneration rate,  $x$  represents the coke conversion,  $t$  represents the regeneration time,  $k$  represents the regeneration rate constant,  $A$  represents the pre-exponential factor,  $E$  represents the regeneration activation energy,  $R$  is the gas constant,  $T$  is the regeneration temperature, and  $f(x)$  is the regeneration model functions depending on the regeneration mechanism. In this work, there are several models used for choosing the regeneration model

function, which are shown in the Table 1.<sup>14,34</sup>  $h(P_{O_2})$  is a function of oxygen partial pressure, which represents the influence of the oxygen concentration on the regeneration rate. As excess oxygen is always used in the experiments,  $P_{O_2}$  can be considered constant. The coke conversion  $x$  is based on

$$x = (W_0 - W_t)/(W_0 - W_f) \quad (2)$$

where  $W_0$  represents the initial mass of the coked catalyst (from 523 K),  $W_t$  represents the mass of the coked catalyst at any time  $t$ , and  $W_f$  represents the mass of the coked catalyst at the end of the reaction. For a constant heating rate,  $T$  can be obtained via

$$T = T_0 + \beta t \quad (3)$$

with  $T_0$  the starting point temperature and  $\beta$  the heating rate. Equation 1 can further be reduced to

$$\beta dx/dT = A \exp(-E/RT)h(P_{O_2})f(x) \quad (4)$$

We can obtain the following expression by rearranging eq 4

$$g(x) = \int_0^x dx/f(x) = [Ah(P_{O_2})E/\beta R]P(u) \quad (5)$$

where  $P(u) = \int_u^\infty e^{-u}/u^2 du$  as well as  $u = E/RT$ . As no analytical solutions are available to the integral of  $P(u)$  in eq 5,<sup>14,35</sup> several approximations have been proposed.

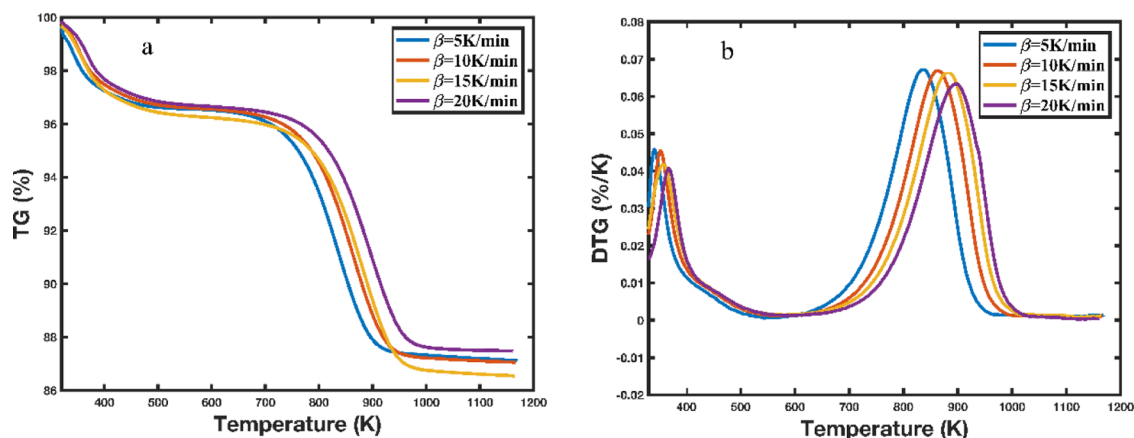


Figure 1. TG (a) and DTG (b) curves for the combustion of coke on industrial MTO catalysts in the air atmosphere.

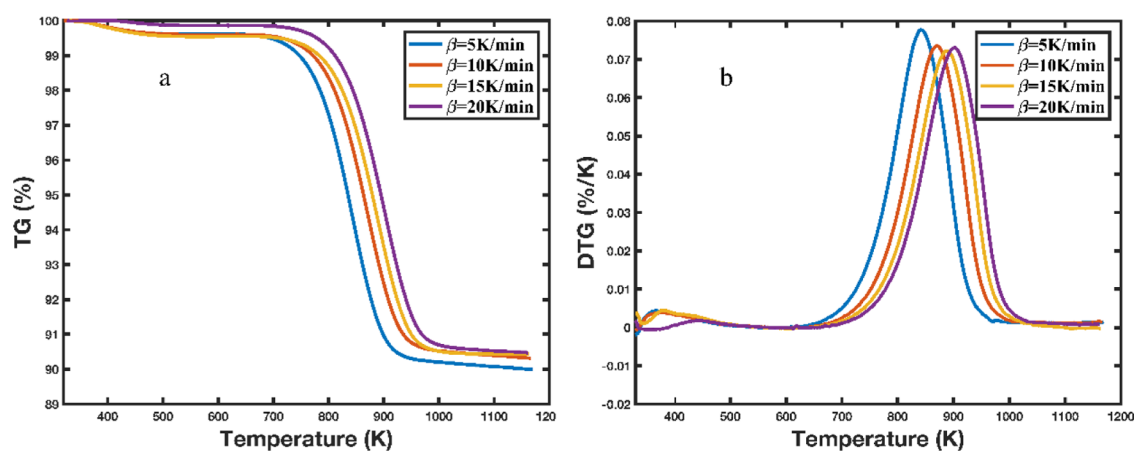


Figure 2. TG and DTG curves for the aging industrial coked MTO catalysts in the air atmosphere.

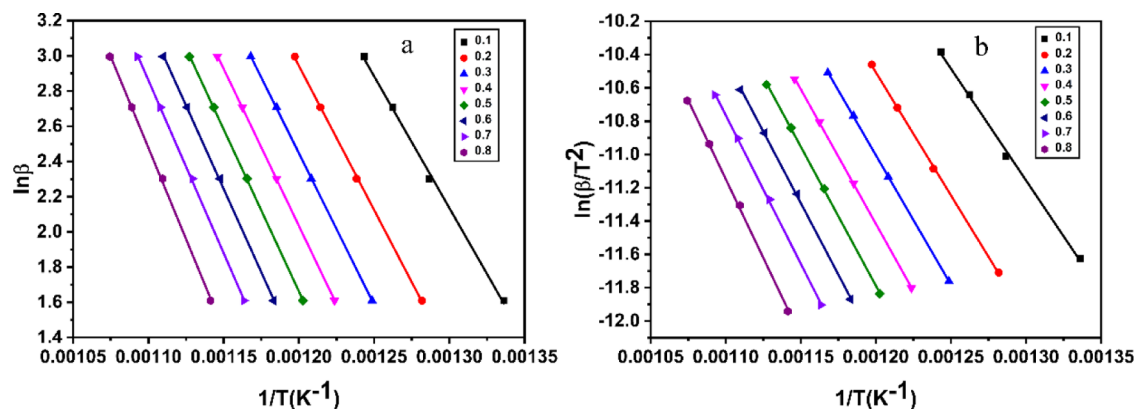


Figure 3. Model-free plots at various conversions of coke  $x$  obtained via FWO (a) and KAS (b) methods for the industrial MTO catalyst.

**3.1. Model-Free Method.** Four different model-free methods were used in this work to achieve regeneration activation energy for the MTO catalyst, which are all presented in Table 2. Detailed descriptions of these methods are included in the Supporting Information.

**3.2. Master-Plot Method.** After the regeneration activation energy  $E$  has been achieved, another important task is choosing a suitable regeneration model function. In this work, we will use the master-plot method. From eq 5, we can obtain:

$$g(x) = (A'E/\beta R)P(u) \quad (10)$$

Note that  $A' = Ah(P_{O_2})$ . Choosing  $x = 0.5$  as a reference point, we can get

$$g(0.5) = (A'E/\beta R)P(u_{0.5}) \quad (11)$$

Then, the master-plot method can be achieved by dividing eq 10 by eq 11.<sup>40</sup>

$$g(x)/g(0.5) = p(u)/p(u_{0.5}) \quad (12)$$

For various regeneration model functions  $g(x)$  from Table 1, we first can obtain different values of  $g(x)/g(0.5)$  at numerous coke conversion values  $x$ . Afterward, we can also obtain

Table 3. Comparison of the Value of  $E$  at Different Conversions of Coke using FWO, KAS, Friedman, and Vyazovkin Methods

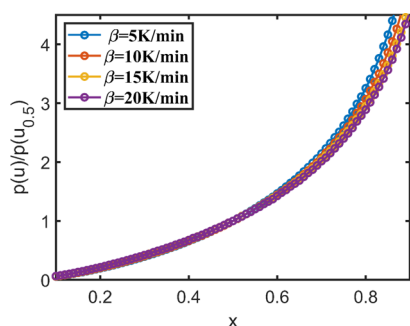
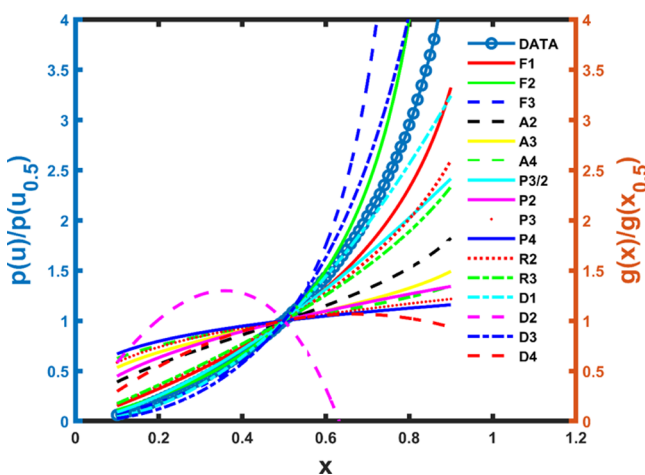
$x$	FWO		KAS		Friedman		Vyazovkin
	$E$ (kJ/mol)	$R^2$	$E$ (kJ/mol)	$R^2$	$E$ (kJ/mol)	$R^2$	$E$ (kJ/mol)
0.1	124.8	0.9871	111.7	0.9843	134.1	0.9957	130.7
0.2	137.0	0.9953	123.4	0.9944	132.8	0.9989	131.9
0.3	144.4	0.9985	130.5	0.9982	135.5	0.9993	134.9
0.4	150.0	0.9993	135.9	0.9992	138.6	0.9962	138.7
0.5	154.5	0.9999	140.1	0.9999	151.7	0.9991	141.8
0.6	160.0	0.9999	145.4	0.9999	151.7	0.9999	145.1
0.7	166.8	0.9999	152.0	0.9999	153.1	0.9973	149.1
0.8	177.4	0.9993	162.3	0.9991	168.9	0.9994	156.7
average	144.3		137.6		145.8		141.1

different values of  $p(u)/p(u_{0.5})$  from the experimental data. From eq 12, we know that  $g(x)/g(0.5)$  will equal  $p(u)/p(u_{0.5})$  when a suitable regeneration model function is chosen. Thus, by comparing the value of  $g(x)/g(0.5)$  from various model functions with the value of  $p(u)/p(u_{0.5})$  from the experimental data, we can obtain suitable regeneration model function for the MTO catalyst.

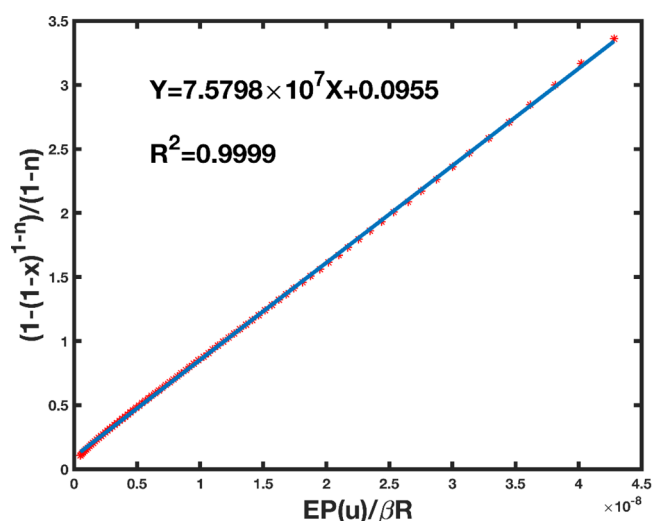
## 4. RESULTS AND DISCUSSION

### 4.1. Impact of Mass Transfer and Heat Transfer.

The combustion of coke on the MTO catalyst includes two

Figure 4.  $p(u)/p(u_{0.5})$  vs  $x$  for four heating rates.Figure 5. Comparison of  $p(u)/p(u_{0.5})$  and  $g(x)/g(x_{0.5})$  at different conversions of coke.

processes, transport and reactions.<sup>7</sup> Therefore, prior to the kinetic analysis, it is necessary to cut down the impact of the transfer process on the experiments results. In general, catalysts with a small mean diameter are used for the regeneration

Figure 6.  $[1 - (1-x)^{1-n}]/(1-n)$  vs  $Ep(u)/\beta R$  at  $n = 1.31$  at a heating rate of 15 K/min.Table 4. Regeneration Kinetic Parameters Gained at Various Values of  $\beta$ 

$\beta$ (K/min)	$A'$ ( $\text{min}^{-1}$ )	$n$	$f(x)$	$R^2$
5	$7.904 \times 10^7$	1.45	$(1-x)^{1.45}$	0.9999
10	$7.740 \times 10^7$	1.34	$(1-x)^{1.34}$	0.9999
15	$7.5804 \times 10^7$	1.31	$(1-x)^{1.31}$	0.9999
20	$7.186 \times 10^7$	1.22	$(1-x)^{1.22}$	0.9999
mean value	$7.602 \times 10^7$	1.33		

kinetics study.<sup>7,41</sup> We evaluated the influence of external diffusion of oxygen by reducing the mass loading of the coked catalyst from 15 to 5 mg while keeping the heating rate and the air flow rate the same. The highly consistent combustion rate of coke with these two mass loadings suggests that the external diffusion of oxygen has a minor influence in this study. To minimize the effect of the internal diffusion, in this work, catalysts with a mean diameter of 80  $\mu\text{m}$  were used. In addition, the Weisz–Prater criterion was applied to assess the impact of the internal diffusion.<sup>33</sup>

$$C_{\text{WP}} = \frac{r_{\text{O}_2} \rho_p R_p^2}{D_e C_{\text{O}_2}}$$

$r_{\text{O}_2}$  represents the oxygen consumption rate (mol/gcat·s),  $\rho_p$  represents the MTO catalyst density (g/dm<sup>3</sup>),  $R_p$  represents the MTO catalyst radius (m).  $D_e$  represents the diffusion coefficient of oxygen (m<sup>2</sup>/s),  $C_{\text{O}_2}$  represents the oxygen

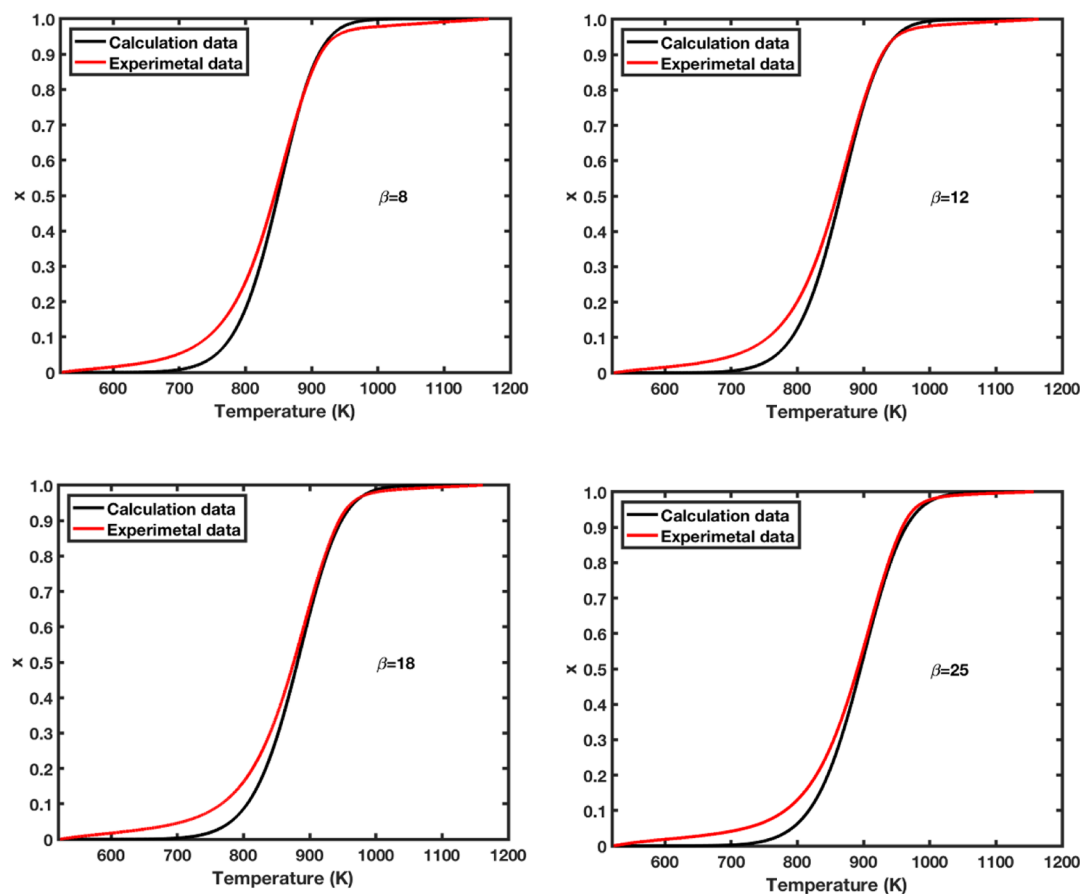


Figure 7. Comparisons between the experimental and the predicted results at different heating rates of 8, 12, 18, and 25 K/min.

concentration ( $\text{mol}/\text{dm}^3$ ). To assess a worst situation, we employed the maximum oxygen consumption rate to achieve the Weisz–Prater criterion. The values are  $r_{\text{O}_2} = 1.32 \times 10^{-5}$   $\text{mol}/\text{gcat}\cdot\text{s}$ ,  $\rho_p = 1500$   $\text{g}/\text{dm}^3$ ,  $R_p = 4 \times 10^{-5}$   $\text{m}$ ,  $D_e = 5 \times 10^{-8}$   $\text{m}^2/\text{s}^9$ , and  $C_{\text{O}_2} = 3.313 \times 10^{-3}$   $\text{mol}/\text{dm}^3$ . The value of  $C_{\text{WP}}$  obtained was 0.1913 ( $<1$ ), which means that oxygen diffusion has no significant effect on combustion. Because catalyst regeneration is an exothermic reaction, to minimize the influence of combustion heat on catalyst temperature, in each run, a small sample weight (15 mg) was used. In addition, the temperature difference between the catalyst surface and the interior was calculated, which is based on the following.<sup>42</sup>

$$\Delta T_{\text{max}} = \frac{-\Delta H_r D_e C_{\text{O}_2}}{\lambda}$$

The combustion enthalpy  $\Delta H_r$  is  $-310$   $\text{kJ}/\text{mol}^6$ , and the oxygen concentration  $C_{\text{O}_2}$  is  $3.313 \times 10^{-3}$   $\text{mol}/\text{dm}^3$ , the diffusion coefficient of oxygen  $D_e$  is  $5 \times 10^{-8}$   $\text{m}^2/\text{s}^9$ , and the thermal conductivity of the catalyst ( $\lambda$ ) is  $1.8$   $\text{J}/\text{s}\cdot\text{m}\cdot\text{K}$ .<sup>43</sup>  $\Delta T_{\text{max}}$  obtained was less than 1 K. Therefore, the temperature increase in the catalyst can be neglected, which means that coke combustion on the catalyst can be considered an isothermal reaction.

#### 4.2. TG and Differential Thermogravimetric Analysis.

A typical thermogravimetric (TG) curve and a differential thermogravimetric (DTG) curve for the combustion of coke on the MTO catalyst under the air atmosphere with different heating rates ( $\beta$ ) are shown in Figure 1. We can see the weight loss rate of the coked MTO catalyst has two peaks, which

indicates there are two stages for the entire combustion process. The first phase is from room temperature to around 523 K corresponding to the mass loss of moisture and a small amount of volatile material. The second phase is from 673 to 1170 K corresponding to coke combustion. It can also be observed in Figure 1 that the maximum combustion rate of the coked catalyst shifts to higher temperature zones as  $\beta$  increases from 5 to 20 K/min. The maximum temperature peaks for different  $\beta$  values are 833, 863, 880, and 897 K. This can be attributed to the thermal hysteresis.<sup>44</sup>

Considering that aging treatment will have a certain effect on coke nature, also the combustion kinetics, we then studied the regeneration of the coked catalysts with  $\text{N}_2$  aging treatment at 773 for 20 min by TGA. Figure 2 presents TG and DTG curves of the aging coked catalyst at different  $\beta$ . As shown in Figure 2, the first desorption peak, corresponding to the mass loss of moisture and volatile material, has almost disappeared for all  $\beta$  during the whole combustion process. This result shows that those moisture and volatile materials can be almost stripped completely under a more severe aging treatment stage. The maximum points of combustion rate occurred at 841, 871, 888, and 901 K for heating rates of 5, 10, 15, and 20 K/min, respectively. Compared with the catalyst without ageing, it can also be observed that the peak temperature at the maximum combustion rate has shifted to higher temperatures for all increasing heating rates. This shift can be attributed to the change of coke nature after  $\text{N}_2$  sweeping treatment.<sup>6</sup>

**4.3. Activation Energy Calculations.** Regeneration activation energy for the coked MTO catalyst was gained using FWO, KAS, Vyazovkin, and Friedman methods. In FWO

and KAS methods, first the regression lines as shown in Figure 3 were plotted. The variations of the value of  $E$  and  $R^2$  at various conversions of the coke are presented in Table 3. Note that the regression lines are also required for calculating the activation energy in the Friedman method, though it is a differential model-free method. From Table 3, it can be observed that for the conversion of coke from 0.1 to 0.8, the value of activation energy is obtained to be 124.8–177.4 kJ/mol using the FWO approach, 111.7–162.3 kJ/mol using the KAS approach, and 130.7–156.7 kJ/mol using the Friedman approach, as well as 134.1–168.9 kJ/mol using the Vyazovkin approach. The results of all model-free methods show a slight increasing trend of  $E$  as the conversion of coke increases, which is consistent with the regeneration of the FCC catalyst reported by Ochoa et al.<sup>9</sup> The evolution of  $E$  at different conversions of coke indicates the existence of complex reactions during the combustion process. According to Ochoa et al.,<sup>9</sup> this may be attributed to the combustion of coke on the deactivated catalyst begins with the light composition then to the heavy composition. As can also be seen, the values of  $E$  calculated using four methods are consistent in general. The deviations of mean values of  $E$  calculated using different methods are within 6.0%. The correlation coefficient ( $R^2$ ) of activation energy calculated using integral methods is normally higher than that obtained using the differential method, that is, the Friedman method, indicating the integral model-free methods are less sensitive to the experimental errors.<sup>14</sup> The mean value of  $E$  obtained (about 141 kJ/mol) is also in consistent with that value obtained by Zhu<sup>7</sup> and is within the range of Aguayo et al. They found combustion activation energy of coke deposited on the SAPO-34 zeolite after aging is between 127 and 151 kJ/mol, which is strongly dependent on the ratio of hydrogen to carbon of coke.<sup>6</sup> However, the activation energy obtained in our study is higher than that reported for the HZSM-5 catalyst.<sup>23,26</sup> This phenomenon was also reported by Aguayo et al. This might be explained by the fact that for the SAPO-34 zeolite with big cavities, the coke deposited on it is of a higher molecular weight and a lower ratio of hydrogen to carbon than that of the HZSM-5 zeolite.<sup>6</sup> In addition, the activation energy of the aging coked catalyst was also calculated, which can be seen in the Supporting Information.

#### 4.4. Determination of Regeneration Model Function.

After regeneration activation energy is calculated, it is necessary to choose an appropriate regeneration model function, which can suitably describe the regeneration process of the industrial MTO catalyst. In this regard, a master-plot method as described using eq 12 was employed to determine the combustion reaction model suitable for the MTO regeneration process. First, considering a reference point at  $x = 0.5$ , we need to calculate the values of  $p(u)/p(u_{0.5})$  for various conversions of coke according to the mean value of  $E$  via the model-free methods as well as the experimental data from four heating rates. In doing so, it is essential to choose a reasonable average value of  $E$  employed in the master-plot method. From Table 3, we can observe the deviation of  $E$  derived by three integral model-free methods is within 10% for each conversion of coke. The average activation energy derived from the Vyazovkin method, that is,  $E = 141.1$  kJ/mol, therefore, is adopted to decide the combustion model function. Figure 4 shows  $p(u)/p(u_{0.5})$  versus  $x$  based on four heating rates. It can be observed that, in general, the experimental masters-plots at various heating rates are consistent. A close

check suggests that a relatively large deviation occurs at a higher conversion of coke, with a decreasing heating rate corresponding to an increasing  $p(u)/p(u_{0.5})$  at a high conversion of coke. This may reflect that the nature of the coke deposited SAPO-34 zeolites changes at different heating rates. A further work to understand such a deviation is subject to future study. Anyway, Figure 4 indicates that the combustion of the coke can be depicted using a suitable reaction model. Moreover, we can also gain the values of  $g(x)/g(0.5)$  at various conversions of the coke according to numerous reaction model functions from Table 1.

According to the above results, we can draw Figure 5, which compares the values of  $p(u)/p(u_{0.5})$  obtained from the experimental results and the values of  $g(x)/g(0.5)$  derived from numerous reaction models at a heating rate of 15 K/min. It can be observed in Figure 5 that the curve of  $p(u)/p(u_{0.5})$  lies between the value of model F1 and model F2, which means that the combustion process of coke on the MTO catalyst can be described using the Fn model, that is, with a model function of  $f(x) = (1 - x)^n$  with  $n$  between 1 and 2.

**4.5. Calculation of the Reaction Order and Pre-Exponential Factor.** Based on the obtained regeneration model function, apparent pre-exponential factor  $A'$  and the reaction order can be determined. The comparison in Section 4.4 shows that the regeneration process of the MTO catalyst can be described using  $f(x) = (1 - x)^n$  and thus

$$g(x) = [1 - (1 - x)^{1-n}]/(1 - n) \quad (13)$$

Combining eqs 10 and 13 can lead to

$$[1 - (1 - x)^{1-n}]/(1 - n) = A'Ep(u)/\beta R \quad (14)$$

According to eq 14, a suitable reaction order can be calculated via a linear fitting left side against the right side by changing  $n$  from 1.0 to 2.0 with a step size of 0.01. The value of reaction order  $n$ , therefore, is the one whose correlation coefficient  $R^2$  is the highest. The plots of  $[1 - (1 - x)^{1-n}]/(1 - n)$  against  $Ep(u)/\beta R$  at  $n = 1.31$ , which correspond to the regeneration process of the coked MTO catalyst at a heating rate of 15 K/min, are shown in Figure 6 as an example. After derivation of  $n$ , the value of  $A'$  can also be acquired from the slope of the lines of  $[1 - (1 - x)^{1-n}]/(1 - n)$  against  $Ep(u)/\beta R$ , as shown in Figure 6. The regeneration kinetic parameters of the coked MTO catalyst, that is, the reaction model, apparent pre-exponential factor, reaction order  $n$ , and correlation coefficient  $R^2$  at four heating rates are presented in Table 4. We obtained a mean value of  $n = 1.33$  and  $A' = 7.602 \times 10^7 \text{ min}^{-1}$ .

**4.6. Comparison of the Predicated Data and Experimental Results.** To validate the feasibility of the acquired regeneration kinetics model, a comparison between the predicted conversion of coke and experimental data has been carried out. Experiments with four additional  $\beta$ , that is, 8, 12, 18, and 25 K/min, were carried out to verify the model. According to eq 4, the following kinetic model of combustion of coke on the MTO catalyst can be acquired

$$dx/dT = A' \exp(-E/RT)f(x)\beta \quad (15)$$

where the following parameters are used to calculate the conversion of coke:  $E = 141.1$  kJ/mol,  $n = 1.33$ , and  $A' = 7.602 \times 10^7 \text{ min}^{-1}$ .

Figure 7 shows the model predictions and experimental results obtained at four additional heating rates. We can find

that the predicted conversion of coke is in accordance with the experimental data for each heating rates. Although at low coke conversion, the experimental results are slightly higher than those of the predicted results, for the whole process, the experimental results are generally consistent with the model predictions. Especially, for the high conversion of coke, which corresponds to the high temperature. Currently, MTO regenerators are industrially overdesigned or oversized because the design is essentially based on the knowledge from industrial FCC practices on the one hand and has a significant margin to ensure smooth operation on the other hand. The lack of industrial MTO catalyst regeneration kinetics apparently hinders the optimization of such design. We believe the obtained kinetic model in this work could favor and improve industrial MTO regenerator design. First, we used industrial MTO catalysts, rather than the zeolite synthesized in laboratory, for the combustion kinetic study. Coking conditions are also consistent with the industrial conditions (e.g., temperature, feed). Second, the temperature we studied covers the operating temperature range in the industrial MTO regenerator. Third, the prediction results with the kinetic model are also consistent with thermogravimetric results for different heating rates. Actually, we are coupling this kinetic model with hydrodynamics to simulate the pilot regenerator in our MTO pilot plant, which, as expected, would be a substantial step toward the establishment of a feasible and reliable kinetic model for industrial MTO regenerator design.

## 5. CONCLUSIONS

In this work, numerous thermogravimetric experiments were conducted under the air atmosphere to study the combustion kinetics of coke for the industrial MTO catalyst. The activation energy for coke combustion was calculated via four model-free methods, including integral and differential methods. The results indicated that the kinetic parameters derived using all model-free methods are quite consistent for any given coke conversion. However, the increase of coke conversion leads to an increase of the corresponding activation energy, which indicates that the light and heavy fractions of coke in the industrial MTO catalyst may have different combustion conditions. An average activation energy for combustion of coke on the industrial MTO catalyst of 141.1 kJ/mol was obtained.

Based on the average activation energy, we used the masterplot method to derive the combustion model function. It is shown that the combustion process of coke for the industrial MTO catalyst can be described using the Fn model. Comparison of the model prediction and the experimental results for other four heating rates, which shows good agreement, demonstrates that the regeneration kinetics could be potentially employed for the design and optimization of MTO regenerators.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c00153>.

Detailed description of model-free methods and the experimental results of the aging treatment catalyst sample (PDF)

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### Notes

The authors declare no competing financial interest.

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