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# TG STUDY OF THE KINETIC PARAMETERS OF REGENERATION OF COKED HZSM-5 ZEOLITE

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## Abstract

A thermogravimetric method is proposed for study of the kinetic parameters of coked HZSM-5 zeolite regeneration. The technique, which makes use of integral thermogravimetric curves, was optimized by microprocessed integrated mathematical methods. The kinetic parameters obtained from the TG curves are the activation energy, the rate constants, the half-life times, and in particular the coke removal time as a function of temperature. The activation energy calculated by using the Flynn and Wall kinetic method was 81.4 kJ $mol^{-1}$. It was observed that, to remove 99% of the coke from the zeolite in a period of 1 h, it would be necessary to carry out thermo-oxidation at 748 K, with a dry air purge flow of 120 $cm^3$ $min^{-1}$.

**Keywords:** catalyst regeneration, HZSM-5 zeolite, thermogravimetry

## Introduction

One of the main causes of catalyst deactivation is the formation and deposition of coke [1], which results from the nucleation of non-reactive polymeric species on the catalyst surface, blocking the channels and cages [2]. Catalyst regeneration is generally achieved by gradual heating under an oxidizing atmosphere [3].

In this work, thermogravimetry (TG) was used to study the kinetic parameters of zeolite regeneration by employing integral TG curves. The kinetic parameters obtained from the TG curves were the activation energy, the rate constants, the half-life times, and in particular the coke removal time as a function of temperature.

## Experimental

The HZSM-5 zeolite was synthesized by refluxing NaZSM-5 zeolite with ammonium chloride solution, followed by calcination at 823 K under a nitrogen flow. The chemical composition of the sample was $Na_{0.29}H_{4.79}Al_{5.08}Si_{90.92}O_{192}$, as determined by atomic absorption spectroscopy.

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The HZSM-5 zeolite catalyst, which is a white powdery solid, was used in the reaction of isomerization of *m*-xylene in a fixed bed continuous flow reactor at 773 K, with a WHSV (weight hourly space velocity) of 50 h$^{-1}$. Under these conditions, after 4 h, the HZSM-5 zeolite catalyst had become deactivated in consequence of coking.

To study the regeneration of the coked catalyst, a DuPont 951 thermobalance was calibrated over all heating rates, using a gas purge, under the same conditions as those applied in the analysis.

Samples of the deactivated catalyst (containing 6.4 mass% of coke) were submitted to pre-treatment under a dry air atmosphere at 303 K. They were then heated in the temperature range 303–1273 K, using heating rates of 2.5, 5.0, 10 or 20 K min$^{-1}$, with a controlled dry air flow of 120 cm$^3$ min$^{-1}$. 0.01 g of coked zeolite was used for each experiment, and all experiments were repeated three times.

## Results and discussion

Determination of the activation energy by using an integral TG curve for a given process involves techniques of low efficiency [4]. Otherwise, differential methods based on the rate of mass loss as a function of the heating temperature are inadequate [5, 6]. Reliable methods for determining the activation energy *E* by using dynamic integral TG curves at several heating rates have been proposed by Ozawa [7] and by Flynn and Wall [8].

Toop [9] developed a relationship to estimate the lifetime of a polymeric material as a function of the temperature. Blaine [10] formulated a correlation between the Toop and the Flynn-Wall methods in software form, by which the lifetimes of different polymeric materials can be determined. The program was used for data processing in respect of the thermo-oxidation of coked H-Y zeolite. A detailed mathematical procedure employed for better software comprehension is as follows.

For a given solid state thermo-oxidation reaction:

$$A_{(s)} \dashrightarrow B_{(g)} \tag{1}$$

where $A_{(s)}$ is the coked catalyst and $B_{(g)}$ represents the oxidation products. The reaction rate can be expressed by [5, 9]

$$\frac{d\alpha}{dt} = f(\alpha)k \tag{2}$$

$$k = \frac{d\alpha}{dtf(\alpha)} \tag{3}$$

where α is the coke fraction decomposed in reaction time *t* and *k* is a constant depending on the absolute temperature *T*.

According to the Arrhenius equation

$$k = Ae^{-E/RT} \tag{4}$$

where $A$ is the pre-exponential factor, $E$ is the activation energy and $R$ is the gas constant. If a linear heating rate β is assumed:

$$T = T_0 + \beta t \tag{5}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta \tag{6}$$

From Eqs (2) and (4):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t f(\alpha)} = A\mathrm{e}^{-E/RT} \tag{7}$$

On substituting Eq. (6) into Eq. (7), we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \left(\frac{A}{\beta}\right) f(\alpha)\mathrm{e}^{-E/RT} \tag{8}$$

As the variables can be separated, Eq. (8) can be integrated:

$$F(\alpha) = \int_0^C \frac{\mathrm{d}\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \int_{T_0}^{T} \mathrm{e}^{-E/RT}\mathrm{d}T \tag{9}$$

$$F(\alpha) = \left(\frac{AE}{\beta R}\right)\left[\frac{\mathrm{e}^{-E/RT}}{E/RT} + \int_{-\infty}^{-E/RT} \frac{\mathrm{e}^{-E/RT}}{E/RT}\mathrm{d}T\right] \tag{10}$$

$$F(\alpha) = \left(\frac{AE}{\beta R}\right) P\left(\frac{E}{RT}\right) \tag{11}$$

or in the logarithmic form:

$$\log F(\alpha) = \log\left(\frac{AE}{RT}\right) - \log\beta + \log P(E/RT) \tag{12}$$

Doyle [11] observed that, when $E/RT \geq 20$, $\log P(E/RT)$ can be obtained via the expression

$$\log P(E/RT) \cong -2.315 - 0.457\left(\frac{E}{RT}\right) \tag{13}$$

Thus, differentiation of Eq. (12) at a constant conversion rate gives

$$\frac{\mathrm{d}\log\beta}{\mathrm{d}1/T} \cong -\left(\frac{0.457}{R}\right)E \tag{14}$$

and, on insertion of the $R$ value 8.314 J $\text{mol}^{-1}$ $\text{K}^{-1}$, an expression is obtained for $E$:

$$E \cong -18.2\frac{d\log\beta}{d(1/T)} \tag{15}$$

It is possible in this way to calculate the activation energy relating to the thermal degradation of a polymer, by using the slope of the logarithmic heating rate curve as a function of reciprocal temperature. This method has been used to evaluate the thermal stability of rigid polyurethane [10], and in studies of coke thermo-oxidation for solid catalyst regeneration [11, 12].

Toop [9] determined a relationship between the activation energy and the estimated lifetime for several polymeric coatings:

$$\ln t_c = \frac{E}{RT_c} + \ln\left[\frac{E}{\beta R}P\left(\frac{E}{RT_p}\right)\right] \tag{17}$$

where $t_c$ is the estimated lifetime, $\beta$ is the heating rate, $E$ is the activation energy, $T_c$ is the temperature to which the system is exposed, $R$ is the gas constant and $T_p$ is the temperature at which the mass loss is 5% [$=f(\beta)$].

With rearrangement of Eq. (17), the temperature of coke removal $T_c$ can be determined for a desired process time:

$$T_c = \frac{E/R}{\ln t_c - \ln\left[\frac{E}{\beta R}P\left(\frac{E}{RT_p}\right)\right]} \tag{18}$$

A plot of this equation shows that a small increment in the oxidation temperature causes a drastic decrease in the time required for catalyst regeneration.

The first step in the TG curve, from 503 to 787 K, is due to hydrocarbons adsorbed during the isomerization reaction (Fig. 1).

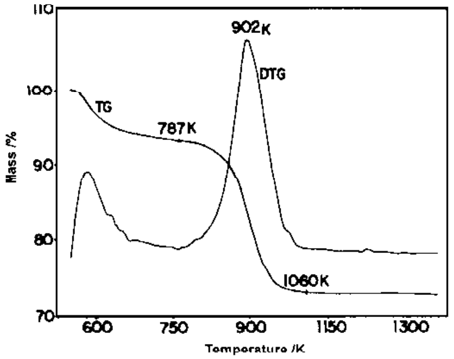

**Fig. 1** TG and DTG curves of coked HZSM-5 zeolite. Heating rate 10 K $\text{min}^{-1}$; dry air flow 120 $\text{cm}^3$ $\text{min}^{-1}$

In order to determine accurately the temperature range of coke thermo-oxidation, the second step in the TG and DTG curves was utilized for each heating rate. For example, with a β value of 10 K $\mathrm{min}^{-1}$, the thermo-oxidation of coke occurs from 787 to 1060 K (Fig. 1).

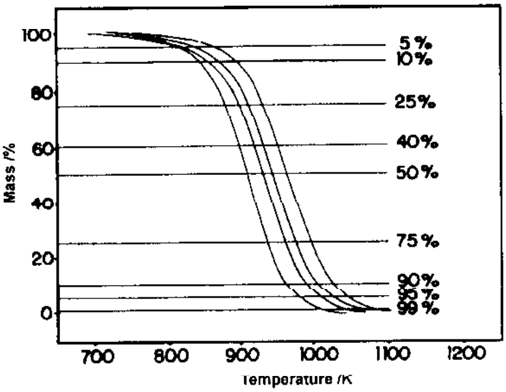

**Fig. 2** Multiple heating rate TG integral curves for different coke removal rates (in %). From left to right: 2.5, 5.0, 10 and 20 K $\mathrm{min}^{-1}$

It may be noted that the thermal region of coke removal is a direct function of the temperature gradient in the samples and is directly proportional to the heating rate employed (Fig. 2), which must be considered for pilot plant estimations. These curves relating to the experiments were reproducible.

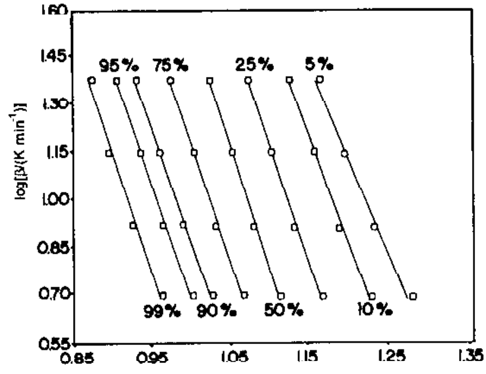

**Fig. 3** Logarithm of heating rate *vs.* reciprocal temperature for different coke removal rates (in %). The activation energy is determined by differentiating these curves

The linearity observed when the logarithm of the heating rate is plotted as a function of reciprocal temperature for several rates of coke degradation (Fig. 3) confirms that the adopted kinetic model can be used to evaluate the removal of the char coating (coke) from catalysts. From the first derivative of these curves, the activation energy $E$ is determined to be 81.4 kJ mol$^{-1}$.

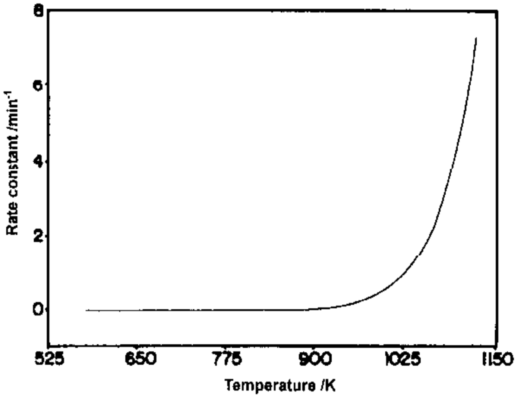

**Fig. 4** Kinetic constant *vs.* temperature for coke oxidation in HZSM-5 zeolite. Heating rate 10 K min$^{-1}$

It is observed that the kinetic constant curve presents almost no variation up to 900 K, at which temperature it rises exponentially, indicating that the velocity of thermo-oxidation increases in the same way after this temperature (Fig. 4).

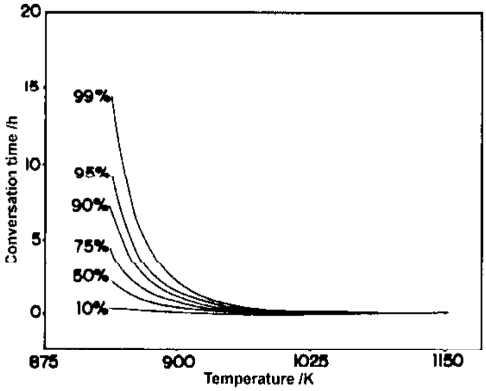

**Fig. 5** Conversion time *vs.* temperature for different coke removal rates (in %) from HZSM-5 zeolite

The times required to reach several percentage conversion rates (10, 50, 75, 95 and 99%) in the thermo-oxidation of coke deposited on HZSM-5 zeolite were calculated, and it was noted that the conversion time decreases considerably as a function of temperature (Fig. 5).

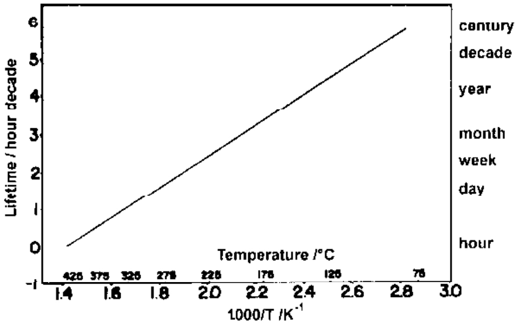

**Fig. 6** Regeneration time of cooked HZSM-5 zeolite *vs*. temperature

From the relationship of Toop [9], it is possible to plot lifetime *vs*. regeneration temperature, allowing a prediction as to how long the removal of coke will take for a given temperature (Fig. 6). This relation can be applied only to the temperature range between 303 and 1000 K, because sintering of the catalyst may occur at higher temperatures [12]. For example, it was observed that, to remove 99% of coke from the zeolite in a period of 1 h, it would be necessary to carry out thermo-oxidation at 748 K, with a dry air purge flow of 120 $cm^3 min^{-1}$.

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