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Kinetic study of H–Y zeolite regeneration by thermogravimetry

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Abstract

The optimized regeneration of coked H–Y zeolite was studied by thermogravimetry using a multiple heating rate integral kinetic method. It was shown that, in order to remove half the coke deposited on zeolite in a period of 1 h, it would be necessary to carry out thermo-oxidation at 742 K. In the same space of time, practically complete regeneration took place at 792 K.

Keywords: Catalyst; Coke; Regeneration; Thermogravimetry; Thermo-oxidation; Zeolite

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1. Introduction

Coke formation is one of the main causes of the deactivation of catalysts [1]. The deposition of coke on zeolites 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, a new thermogravimetric method is proposed for studying the kinetic parameters of zeolite regeneration. The technique uses integral thermogravimetric curves and was optimized by recent microprocessed integrated mathematical methods. The kinetic parameters obtained from TG curves are: activation energy, rate constants, half-life times and, in particular, the coke removal time as a function of temperature.

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2. Experimental

The H–Y zeolite was synthesized by refluxing NaY zeolite ($SiO_2Al_2O_3 = 2.4$) with ammonium chloride solution, followed by calcination at 773 K under nitrogen flow. The chemical composition of the sample, as determined by atomic absorption, was $Na_{19.4}H_{37.6}(AlO_2)_{57}(SiO_2)_{135}$.

The H–Y zeolite catalyst, which is a white powdery solid, was used in the reaction of alkylation of benzene with dodecene in a fixed bed continuous flow reactor at 573 K, with WHSV (Weight Hourly Space Velocity) of 23.5 h^{-1}. Under these conditions, after 1 h, the H–Y zeolite catalyst had become deactivated by coking.

To study the regeneration of the coked catalyst, a Du Pont 910 thermobalance was calibrated over all heating rates, using a gas purge, in the same conditions as those of the analysis.

Samples of the deactivated catalyst (containing 27.7 wt% of coke) were submitted to a 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 and 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.

3. Results and discussion

The determination of the activation energy using an integral TG curve for a given process involves techniques of low efficiency [4]. Also, 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 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 method in software form, by which can be determined the lifetime of different polymeric materials. 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

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

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

$$\frac{\partial C}{\partial t} = f(C)k \tag{2}$$

$$k = \frac{\partial C}{\partial t f(C)} \tag{3}$$

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

According to the Arrhenius equation

$$k = A \exp[-E/(RT)] \tag{4}$$

where A is the pre-exponential factor, E is the activation energy and R is the gas constant.

Assuming a linear heating rate β, so that

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

leading to

$$\frac{\partial T}{\partial t} = \beta \tag{6}$$

Applying Eq. (2) in Eq. (4)

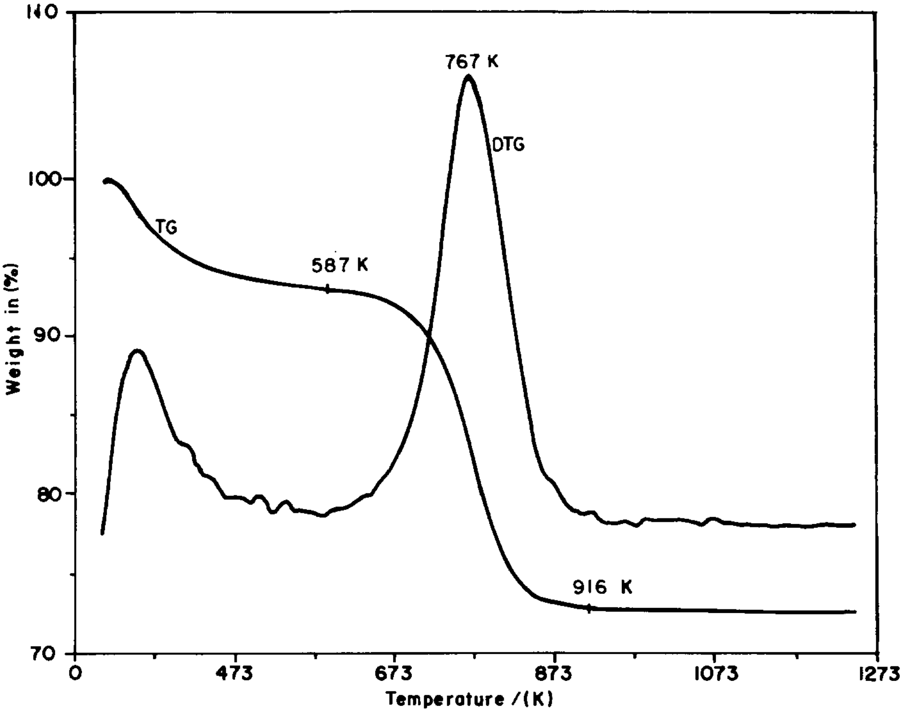

Fig. 1. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of coked H–Y zeolite. Heating rate 10 K min^{-1}; dry air flow 120 cm^3 min^{-1}.

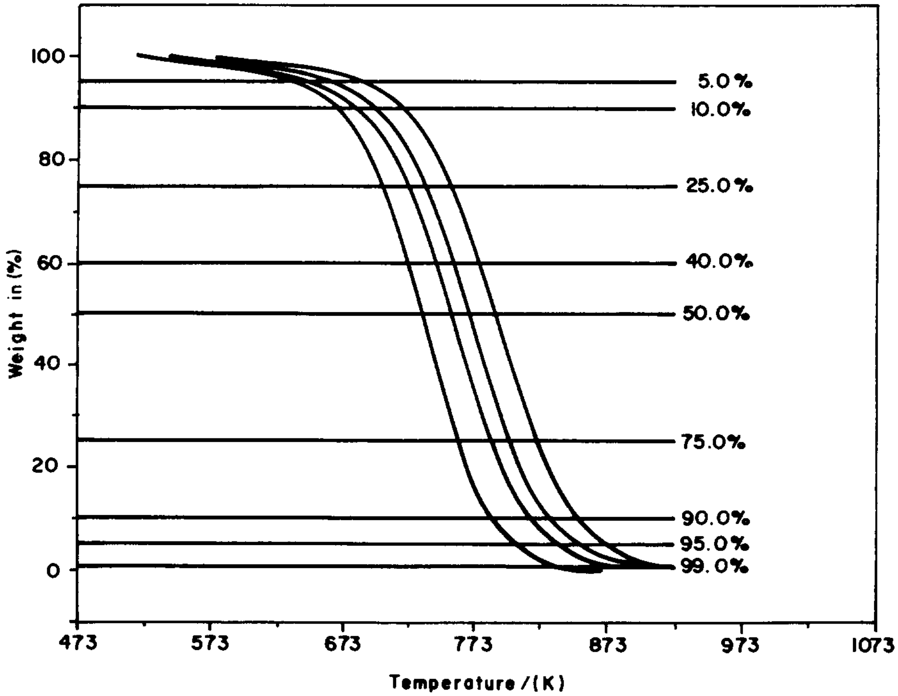

Fig. 2. Multiple heating rate thermogravimetric integral curves for different coke removal rates (in %). From left to right: 2.5, 5.0, 10 and 20 K min^{-1}.

$$\frac{\partial C}{\partial t f(C)} = A \exp[-E/(RT)] \tag{7}$$

Substituting Eq. (6) in Eq. (7), we obtain

$$\frac{C}{T} = \left(\frac{A}{\beta}\right) f(C) \exp[-E/(RT)] \tag{8}$$

Supposing that $A, E, f(C) \neq g(T)$ and $A, E \neq h[f(C)]$, then the variables can be separated and Eq. (8) can be integrated.

$$F(C) = \int_0^C \frac{\partial C}{f(C)} = \left(\frac{A}{\beta}\right) \int_{T_0}^{T} \exp[-E/(RT)] \partial T \tag{9}$$

$$F(C) = \left(\frac{AE}{\beta R}\right) \left[\frac{\exp[-E/(RT)]}{E/(RT)} + \int_{-\infty}^{-E/(RT)} \frac{\exp[E/(RT)]}{(E/RT)} \partial(E/RT) \right] \tag{10}$$

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

or in logarithmic form

$$\log F(C) = \log(AE/RT) - \log\beta + \log P(E/RT) \tag{12}$$

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

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

So Eq. (12) becomes

$$\log F(C) \cong \log(AE/R) - \log\beta - 2.315 - 0.457(E/RT) \tag{14}$$

Differentiation of Eq. (14) at a constant conversion rate gives

$$\frac{\partial \log\beta}{\partial(1/T)} \cong -\left(\frac{0.457}{R}\right)E \tag{15}$$

and, inserting the R value 8.314 J mol^{-1} K^{-1}, an expression is obtained for E

$$E \cong -18.2\frac{\partial \log\beta}{\partial(1/T)} \tag{16}$$

It is thus possible to calculate the activation energy related to thermal degradation of an organic residue, using the slope of the logarithmic heating rate curves as a function of reciprocal temperature.

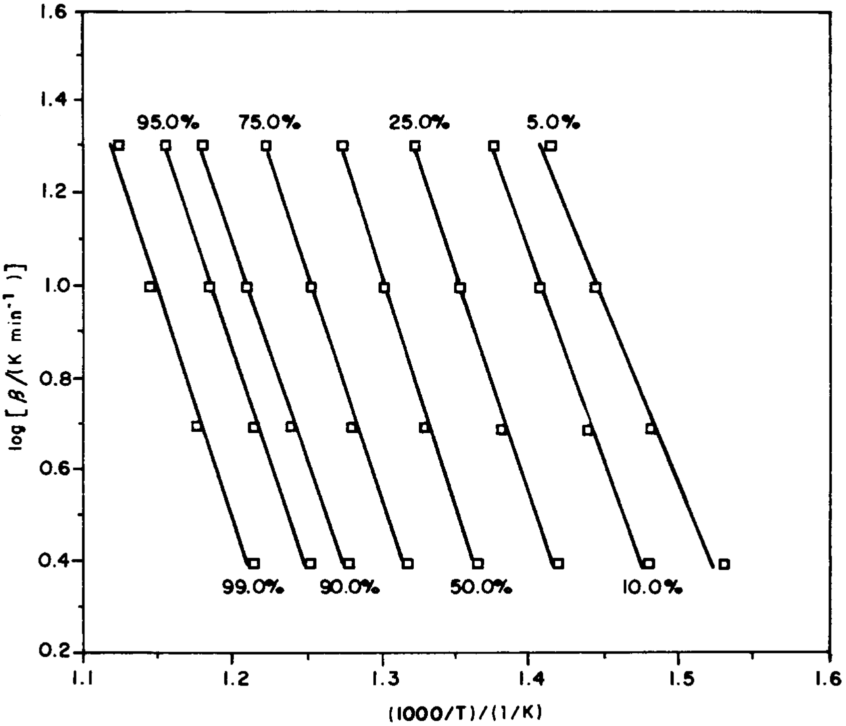

Fig. 3. Logarithm of heating rate versus the reciprocal temperature for different coke removal rates (in %). The activation energy is determined by differentiating these curves.

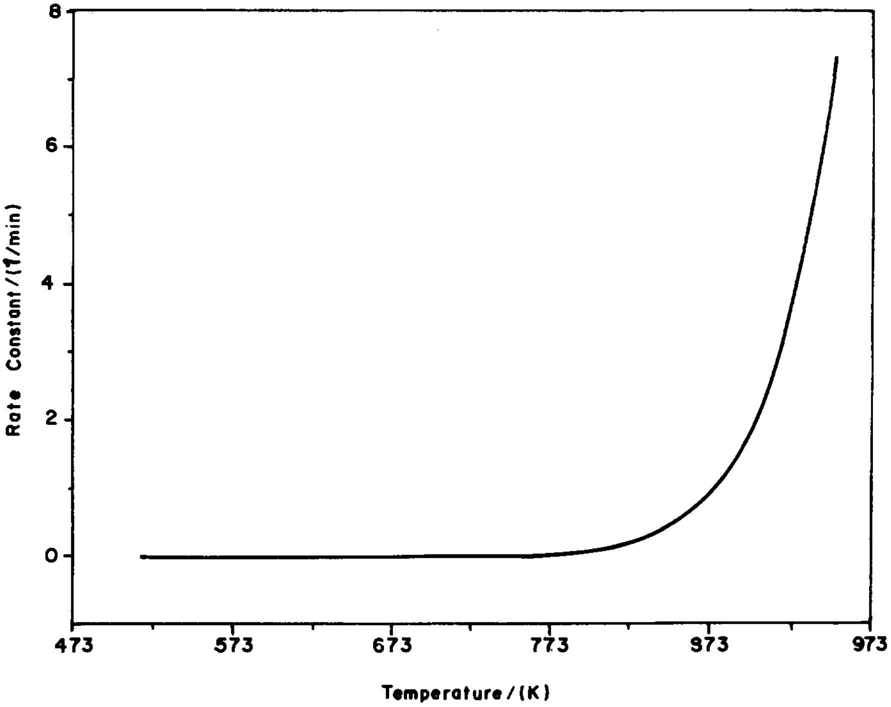

Fig. 4. Kinetic constant versus temperature for the coke oxidation in H–Y zeolite. Heating rate 10 K min^{-1}.

Toop [9] determined a relationship between 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, β 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% $[=f(\beta)]$.

Reorganizing Eq. (17), the temperature for coke removal T_c can be determined for a desired process time

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

Plotting 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 303 to 587 K, is due to hydrocarbons adsorbed during the alkylation reaction (Fig. 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, using a β value of 10 K min^{-1}, the thermo-oxidation of coke occurs from 587 to 916 K (Fig. 1).

It can be noted that the thermal region of coke removal is a direct function of the temperature gradient in the samples and 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.

The linearity observed when the logarithm of heating rate is plotted as a function of reciprocal temperature for several degradation rates of coke (Fig. 3) confirms that the adopted kinetic model can be used to evaluate the removal of char coating (coke) from catalysts. From the first derivative of these curves the activation energy E is determined as being 183.1 (kJ mol^{-1}).

It is observed that the kinetic constant curve presents almost no variation up to 773 K, at which temperature it rises exponentially, indicating that the velocity of thermo-oxidation increases in the same way after this temperature (Fig. 4).

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

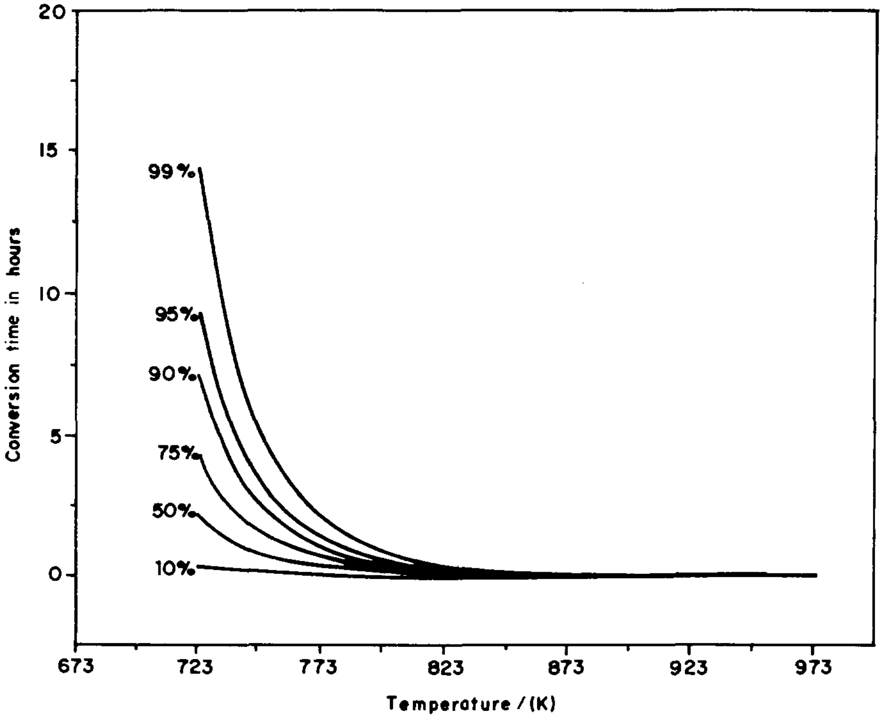

Fig. 5. Conversion time versus temperature for different coke removal rates (in %) of H–Y zeolite.

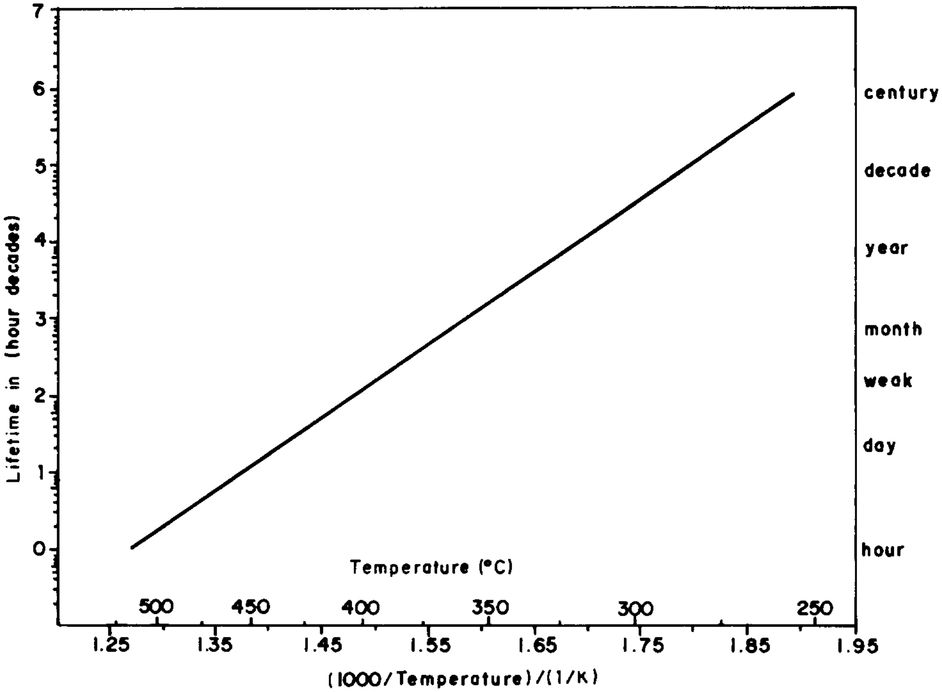

Fig. 6. Regeneration time of coked H–Y zeolite versus temperature.

From the relationship of Toop [9] it is possible to plot lifetime versus regeneration temperature, allowing us to predict how long the removal of coke will take for a given temperature (Fig. 6). This relation can only be applied to a temperature range between 303 and 1000 K because sintering of the catalyst may occur at higher temperatures [12]. For instance, it was observed that, to remove 99% of coke from zeolite in a period of one hour, it would be necessary to carry out thermo-oxidation at 791 K, with a dry air purge flow of 120 (cm^3 min^{-1}).

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