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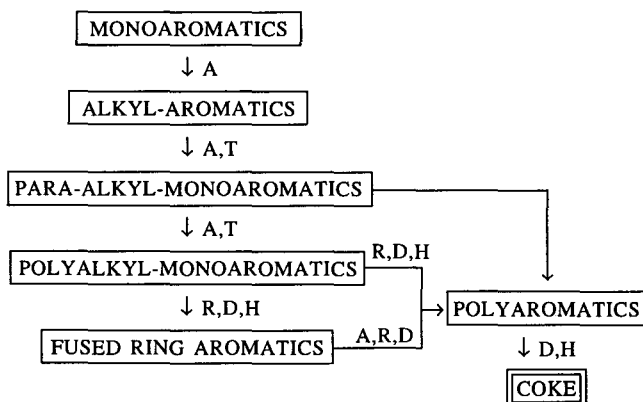
The optimized regeneration of coked H-Y zeolite, employed in benzene alkylation, was studied by thermogravimetry, using a multiple heating rate integral kinetic method. It is shown that in order to remove half of the coke deposited on zeolite, in a period of one hour, it would be necessary to process thermoxidation at 742 K. In the same time, practically the full regeneration takes place at 792 K.

Keywords: H-Y zeolite regeneration; coke thermoxidation kinetics; multiple heating rate TG method.

INTRODUCTION

Catalysts usage is widespread for numerous important processes in chemical and petroleum processing industries. Most catalysts, unfortunately, suffer a loss of activity with time on stream and the life of even the most robust catalyst is limited.

Coke formation is one of the main reasons for catalyst deactivation¹. The coke deposition on zeolites results from the non-reactive polymeric species nucleation on the catalyst surface, blocking the channels and cages². Coke formation on H-Y zeolite during benzene alkylation with olefins to produce alkyl-monoaromatics is the following³:



Scheme 1. Schematic representation of the mechanisms responsible for the formation of carbonaceous deposits.

A = Alkylation; D = Dehydrogenation; R = Cyclization; H = Hydrogen transfer; T = Transalkylation.

It is generally agreed by all investigators that the molecular formula of the coke deposit varies between $C_1H_{0.4}$ and C_1H_1 ⁴. This demonstrates that significant quantities of hydrogen are present, so the oxidation will produce CO_2 , CO and appreciable quantities of water vapor. The catalyst regeneration is generally achieved by gradual heating under oxidizing atmosphere⁵.

In this work, a new thermogravimetric method to study the kinetic parameters of zeolite regeneration is proposed; the technique uses integral thermogravimetric curves and it was optimized by recent microprocessed integrated mathematical methods. The kinetic parameters obtained from TG curves are: activation energy, rate constants, half-life times and, mainly, the coke removal time as a function of temperature.

EXPERIMENTAL

The catalyst studied was a coked H-Y zeolite, used in benzene alkylation with a 1:1:1 molar mixture of C_{10} , C_{11} and C_{12} linear alkenes. This reaction was carried out in an integral tubular fixed bed reactor, with WHSV (weight hourly space velocity) of 20 h^{-1} , at 350°C for one hour.

A DuPont 910 thermobalance was calibrated for all of the heating rates, using gas purge, in the same conditions observed during the analysis.

The samples of the coked catalyst were taken as soon as the reactor reached room temperature (containing 27.7% of coke, by weight) and then submitted to a pretreatment under dry air, at 303 K. These samples were heated in the temperature range of 303 to 1273 K, employing the following heating rates: 2.5; 5.0; 10 and $20\text{ K}\cdot\text{min}^{-1}$, and a controlled dry air flow of $120\text{ cm}^3\cdot\text{min}^{-1}$.

RESULTS

The determination of the activation energy using an integral TG curve of a given process, involves techniques of low efficacy⁶. Also, differential methods based in the mass loss velocity in function of the heating temperature are deficient^{7,8}.

Reliable methods to determine the activation energy (E) using dynamic integral TG curves at several heating rates were proposed by Osawa⁹ and by Flynn and Wall¹⁰. Toop¹¹ developed a relation to estimate lifetime of a polymeric material in function of the temperature. Blaine¹² related a correlation between Toop and Flynn/Wall methods in a software form, in which the lifetime of different polymeric materials can be determined. The program was used to the data processing referent to the coked H-Y zeolite thermoxidation. A detailed mathematical procedure employed for a better software comprehension is the following:

For a given solid state thermoxidation reaction:



the reaction rate can be expressed by^{7, 10}:

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

or

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

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

According to the Arrhenius equation,

$$k = A \cdot e^{-E/(R \cdot T)} \quad (4)$$

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

Supposing that a linear heating rate (β), so that:

$$T = T_0 + \beta \cdot t \quad (5)$$

$$\frac{\partial T}{\partial t} = \beta \quad (6)$$

Applying (2) in (4):

$$\frac{\partial C}{\partial t \cdot f(C)} = A \cdot e^{-E/(R \cdot T)} \quad (7)$$

Substituting (6) in (7) observes:

$$\frac{\partial C}{\partial t} = \left(\frac{A}{\beta}\right) \cdot f(C) \cdot e^{-E/(R \cdot T)} \quad (8)$$

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

$$F(C) = \int_0^C \frac{\partial C}{f(C)} = \left(\frac{A}{\beta}\right) \int_{T_0}^T e^{-E/(R \cdot T)} \cdot \partial T \quad (9)$$

$$F(C) = \left(\frac{A \cdot E}{\beta \cdot R}\right) \cdot \left[\frac{e^{-E/(R \cdot T)}}{E/(R \cdot T)} + \int_{-\infty}^{-E/(R \cdot T)} \frac{e^{E/(R \cdot T)}}{(E/R \cdot T)} \partial(E/R \cdot T) \right] \quad (10)$$

$$F(C) = \left(\frac{A \cdot E}{\beta \cdot R}\right) \cdot P(E/R \cdot T) \quad (11)$$

in logarithmical form:

$$\log F(C) = \log(A \cdot E/R) - \log \beta + \log P(E/R \cdot T) \quad (12)$$

Doyle¹³ observed when $E/R \cdot T \geq 20$, $\log P(E/R \cdot T)$ can be obtained by the expression:

$$\log P(E/R \cdot T) \approx -2,315 - 0,457 \left(\frac{E}{R \cdot T}\right) \quad (13)$$

So, equation (12) becomes:

$$\log F(C) \approx \log \left(\frac{A \cdot E}{R}\right) - \log \beta - 2,315 - 0,457 \cdot \left(\frac{E}{R \cdot T}\right) \quad (14)$$

Derivation of equation (14) at a constant conversion rate gives:

$$\frac{\partial \log \beta}{\partial 1/T} \approx - \left[\frac{0,457}{R} \right] \cdot E \quad (15)$$

Inserting R value, $1,987 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$, it is obtained a expression for E:

$$E \approx -4,35 \frac{\partial \log \beta}{\partial 1/T} \quad (16)$$

Therefore, it is possible to calculate the activation energy related to organic residue thermal degradation, using the inclination of heating rate logarithmical curves as a function of reciprocal temperature.

Toop¹¹ determined a relation between *activation energy* and the *estimated lifetime* for several polymeric coatings.

$$\ln t_c = \frac{E}{R \cdot T_c} + \ln \left[\frac{E}{\beta \cdot R} \cdot P \left(\frac{E}{R \cdot T_p} \right) \right] \quad (17)$$

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

Reorganizing equation (17), the temperature for coke remotion (T_c) for a desired process time can be calculated.

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

This equation plotting shows that a small increment in the oxidation temperature causes a drastic decrease in the time required for catalyst regeneration.

In order to determine the accurate temperature range of coke thermoxidation, differential thermogravimetric curves were utilized, in each heating rate. For example, using a β value of $10 \text{ K} \cdot \text{min}^{-1}$, coke thermoxidation occurs between 587 and 916 K (Fig.1), without affecting the zeolite framework. It can be noted that the thermal region of coke remotion is a direct function of the employed heating rate (Fig.2), which must be considered for pilot plant estimations.

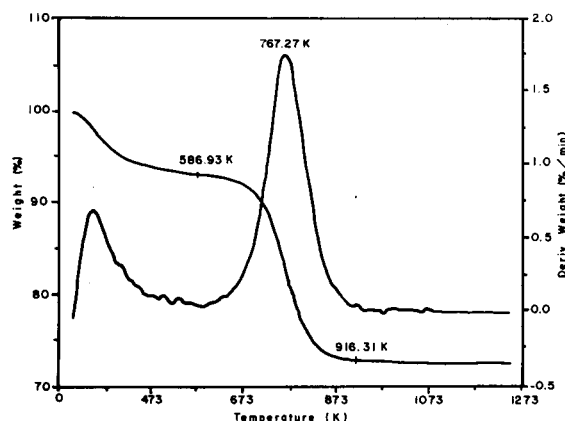


Figure 1. Differential thermogravimetric curve of coked Y zeolite, heating rate of $10 \text{ K} \cdot \text{min}^{-1}$, dry air flow of $120 \text{ cm}^3 \cdot \text{min}^{-1}$.

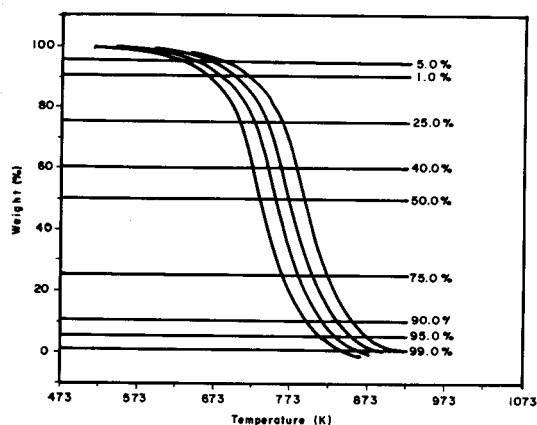


Figure 2. Multiple heating rates thermogravimetric integral curves. From left to right: 2.5, 5.0, 10 and $20 \text{ K} \cdot \text{min}^{-1}$.

The linearity observed when 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 char coating (coke) remotion of catalyst. From the first derivative of these curves activation energy (E) is determined: 183.1 KJ.mole⁻¹.

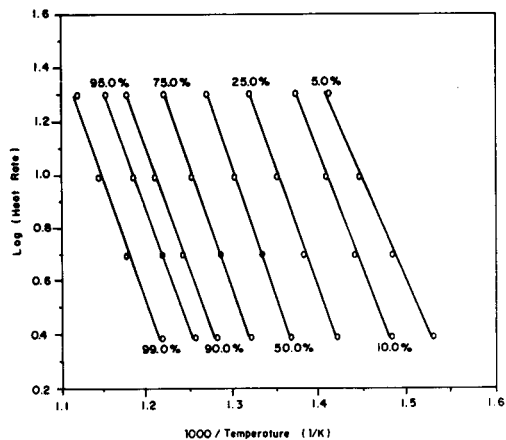


Figure 3. Logarithm of heating rate versus reciprocal temperature. Activation energy was determined by deriving these curves.

It is observed that the kinetic constant curve presents almost no variation up to 773 K when, it raises exponentially, indicating that thermoxidation velocity increases in the same way after this temperature (Fig.4). The time required to reach several percentage conversion rates (10, 50, 75, 95 e 99%) in the thermoxidation of deposited coke on H-Y zeolite was calculated, noting that conversion time considerably decreases in function of temperature (Fig.5).

From Toop's relation¹¹ it is possible to plot lifetime versus regeneration temperature, allowing to predict how long coke remotion will take for a given temperature (Fig.6). It was observed that, for instance, to remove 99% of coke from zeolite, in a period of one hour, it would be necessary to process thermoxidation at 791K, with a dry air purge of 120 cm³.min⁻¹.

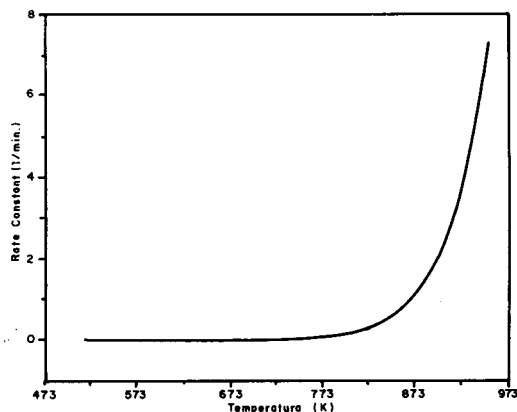


Figure 4. Kinetic constant versus temperature to the coke thermoxidation in H-Y zeolite.

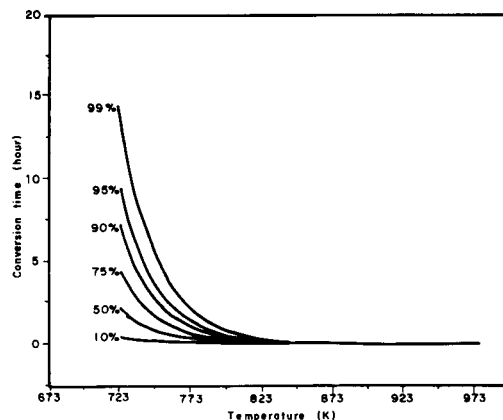


Figure 5. Conversion time versus temperature for different coke remotion rates of coked H-Y zeolite.

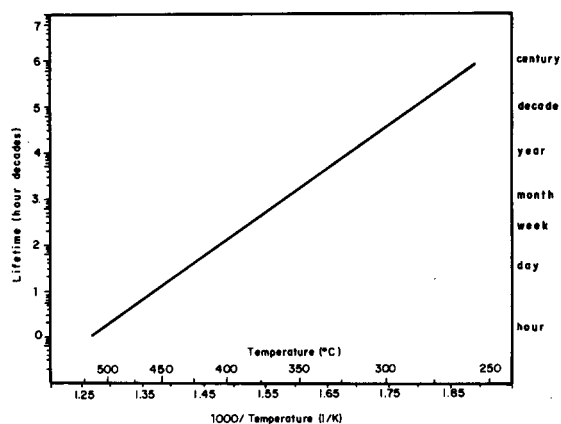


Figure 6. Regeneration time of coked H-Y zeolite versus temperature.

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