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 cm³ 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 Na₀.2H₄.79Al₅.08Si₉₀.92O₁₀₂, 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 cm³ 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 adequate [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:

\[ A_{(s)} \rightarrow B_{(g)} \]  \hspace{1cm} (1)

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

\[ \frac{d\alpha}{dt} = f(\alpha)k \]  \hspace{1cm} (2)

\[ k = \frac{d\alpha}{dt(\alpha)} \]  \hspace{1cm} (3)

where \( \alpha \) 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

\[ k = Ae^{-E/RT} \]  \hspace{1cm} (4)

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