

# Model-free kinetics applied to regeneration of coked alumina

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## Abstract

Thermogravimetry is proposed for studying the alumina catalyst regeneration deactivated by coke, after being used in the transformation of styrene in a fixed bed continuous flow reactor. The model-free kinetic approach has been applied to data for thermal oxidation of carbonaceous deposits on the catalyst. The activation energy ( $E$ ) was calculated as a function of conversion ( $\alpha$ ) and temperature ( $T$ ), by using Vyazovkin model-free kinetic method, allowing to estimate time required to remove coke for a given temperature.

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## 1. Introduction

One of the major problems related to the operation of heterogeneous catalysis is the catalyst loss of activity with time-on-stream, denominated deactivation. Mechanisms of carbon deposition and coke formation on catalysts have been detailed in several reviews [1–4]. One of the main causes of catalysts deactivation is formation and deposition of coke [5], which results from the nucleation of non-reactive polymeric species on the catalyst surface, blocking the channels and cages [6]. Catalyst regeneration is generally achieved by gradual heating under oxidizing atmosphere [7]. In this work, thermogravimetry is used for studying the kinetic parameters of alumina regeneration employing integral TG curves and a model-free kinetic method to calculate the activation energy, the conversion rates and, in particular, the coke removal time as a function of temperature.

## 2. Experimental

The alumina catalyst was synthesized by the impregnation method with aluminum nitrate solution, followed by calcination at 823 K under nitrogen flow. The resulting catalyst, which is a white powdery solid was used in the transformation of styrene in a fixed bed continuous flow reactor at 450 °C, with weight hourly space velocity (WHSV) of 50 h<sup>-1</sup>, for 4 h. Under these conditions, the catalysts had become deactivated by coking.

To study the regeneration of the coked catalyst, a Mettler TG/SDTA 851 thermobalance was calibrated over all heating rates, using a gas purge, in the same conditions as those of the analysis.

Samples of the deactivated catalysts, containing 17.0% (w/w) of organics, were submitted to a pre-treatment under a dry air atmosphere at 30 °C. They were then heated in the temperature range 30–900 °C using heating rates of 5.0, 10 and 20 °C min<sup>-1</sup>, with a controlled dry air flow of 120 cm<sup>3</sup> min<sup>-1</sup>. 0.01 g of coked catalyst was used for each experiment.

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### 3. Results and discussion

The reaction rate of a chemical reaction depends on conversion ( $\alpha$ ), temperature ( $T$ ) and time ( $t$ ). The reaction rate represented as a function of conversion  $f(\alpha)$  is different for each process and must be determined experimentally. For simple reactions, the evaluation of  $f(\alpha)$  with the  $n$ th order is possible. For complex reactions the function of ( $\alpha$ ) is complicated and generally unknown; in this cases the  $n$ th order algorithm causes unreasonable kinetic data. With the model-free kinetics more accurate evaluations of complex reactions can be performed, as a trustworthy way of obtaining reliable and consistent kinetic information about the overall process [8].

Vyazovkin [9,10] developed an integral kinetic method where no model has to be selected (model free-kinetics) which allows to evaluate both simple and complex reactions, using multiple heating rates. The theory is based on that  $(\partial\alpha/\partial T) = k e^{-E/RT} f(\alpha)$  and that the activation energy  $E(\alpha)$  is constant for a certain conversion (isoconversional method).

A chemical reaction is measured at least at three different heating rates ( $\beta$ ) and the respective conversion curves are calculated out of the TG measured curves.

For each conversion  $\alpha$ ,  $\ln(\beta/T_\alpha^2) e$  plotted versus  $(1/T_\alpha)$ , giving a straight line with the slope  $(-E_\alpha/R)$ , therefore the activation energy is obtained as a function of conversion.

Taking the reaction rate equation, presented as  $f(\alpha)$ , and dividing by the heating rate  $\beta = dT/dt$ :

$$\frac{\partial\alpha}{\partial t} = kf(\alpha) \rightarrow \frac{\partial\alpha}{\partial T} = \frac{k}{\beta}f(\alpha) \quad (1)$$

where:  $(\partial\alpha/\partial t)$  is the reaction rate ( $s^{-1}$ );  $k$  is velocity constant ( $s^{-1}$ );  $\alpha$  is conversion;  $\beta$  is the heating rate ( $K s^{-1}$ ). Substituting  $k$  by the Arrhenius expression  $k = k_0 e^{-E/RT}$  and rearranging gives:

$$\frac{1}{f(\alpha)}\partial\alpha = \frac{k_0}{\beta} e^{-E/RT}\partial T \quad (2)$$

Integrating up to conversion,  $\alpha$  (at the temperature  $T$ ) gives:

$$\int_0^\alpha \frac{1}{f(\alpha)}\partial\alpha = g(\alpha) = \frac{k_0}{\beta} \int_{T_0}^T e^{-E/RT}\partial T \quad (3)$$

Since  $E/2T \gg > 1$ , the temperature integral can be approximated by:

$$\int_{T_0}^T e^{-E/RT}\partial T \approx \frac{R}{E} T^2 e^{-E/RT} \quad (4)$$

Substituting the temperature integral, rearranging and logarithming, gives:

$$\ln \frac{\beta}{T_\alpha^2} = \ln \left[ \frac{Rk_0}{E_\alpha g(\alpha)} \right] - \frac{E_\alpha}{R} \frac{1}{T_\alpha} \quad (5)$$

This is defined as dynamic equation, which is used for the determination of the activation energy for all conversion values ( $\alpha$ ).

The first step in the TG curve, from 30 to 450 °C, is due to hydrocarbons adsorbed during the cracking reaction (Fig. 1).

In order to determine accurately the temperature range of coke thermal oxidation, the second step in the TG and DTG curves was utilized for each heating rate.

Table 1  
Temperature for removing coke as a function of time, for different conversions

Time (min)	Temperature (°C)					
	10%	25%	50%	75%	90%	95%
60	235.30	290.72	374.76	432.51	–	–
120	222.34	275.01	360.10	416.12	–	–
180	215.07	266.22	351.83	406.88	–	–
240	210.03	260.15	346.09	400.47	–	–
300	206.20	255.54	341.72	395.58	445.62	–
360	203.11	251.83	338.19	391.64	441.55	–
420	200.53	248.73	335.23	388.34	438.15	–
480	–	246.07	332.69	385.52	435.22	–
540	–	243.76	330.47	383.04	432.67	–
600	–	241.70	328.50	380.84	430.39	–
660	–	239.85	326.73	378.87	428.35	–
720	–	238.18	325.12	377.07	426.49	–
780	–	236.65	323.65	375.43	424.80	–
840	–	235.24	322.29	373.92	423.23	–
900	–	233.94	321.03	372.52	421.78	–
960	–	232.72	319.86	371.21	420.43	–
1020	–	231.59	318.77	369.99	419.16	–
1080	–	230.52	317.74	368.84	417.97	–
1140	–	229.52	316.76	367.76	416.85	–
1200	–	228.57	315.85	366.74	415.79	–
1260	–	227.67	314.97	365.77	414.79	–
1320	–	226.82	314.15	364.84	413.83	–
1380	–	226.00	313.36	363.97	412.92	–
1440	–	–	–	–	–	–

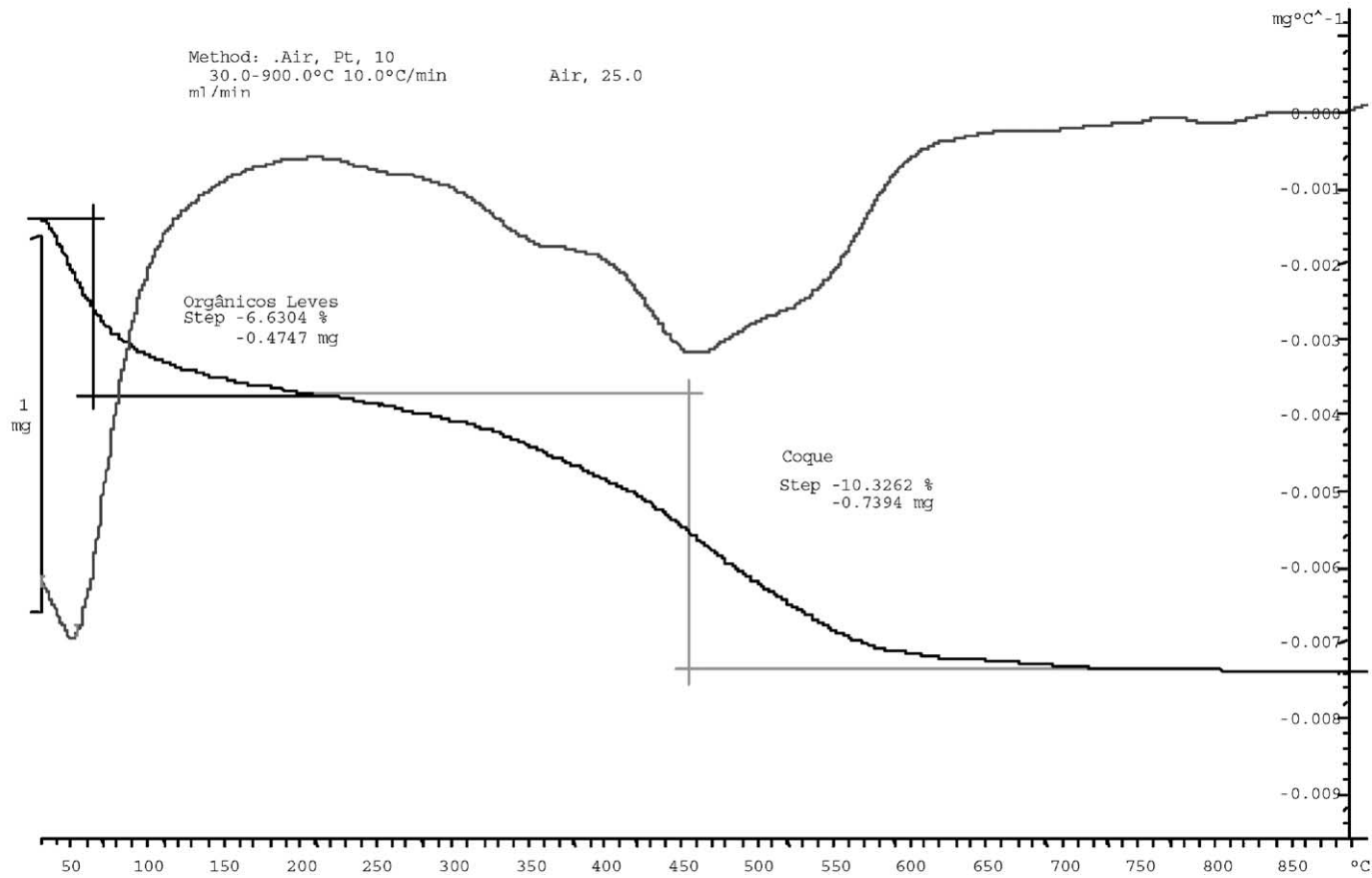


Fig. 1. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of coked alumina. Heating rate 10 K min<sup>-1</sup>; dry air flow 120 cm<sup>3</sup> min<sup>-1</sup>.

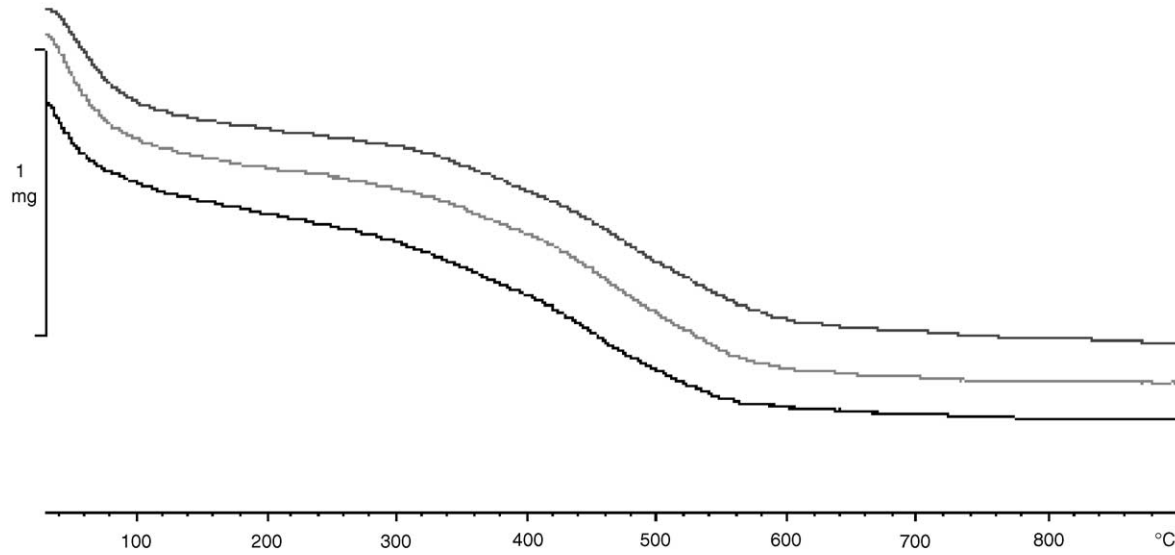


Fig. 2. Multiple heating rate thermogravimetric integral curves for different coke removal rates in percentage (w/w). From left to right: 5.0, 10 and 20 K min<sup>-1</sup>.

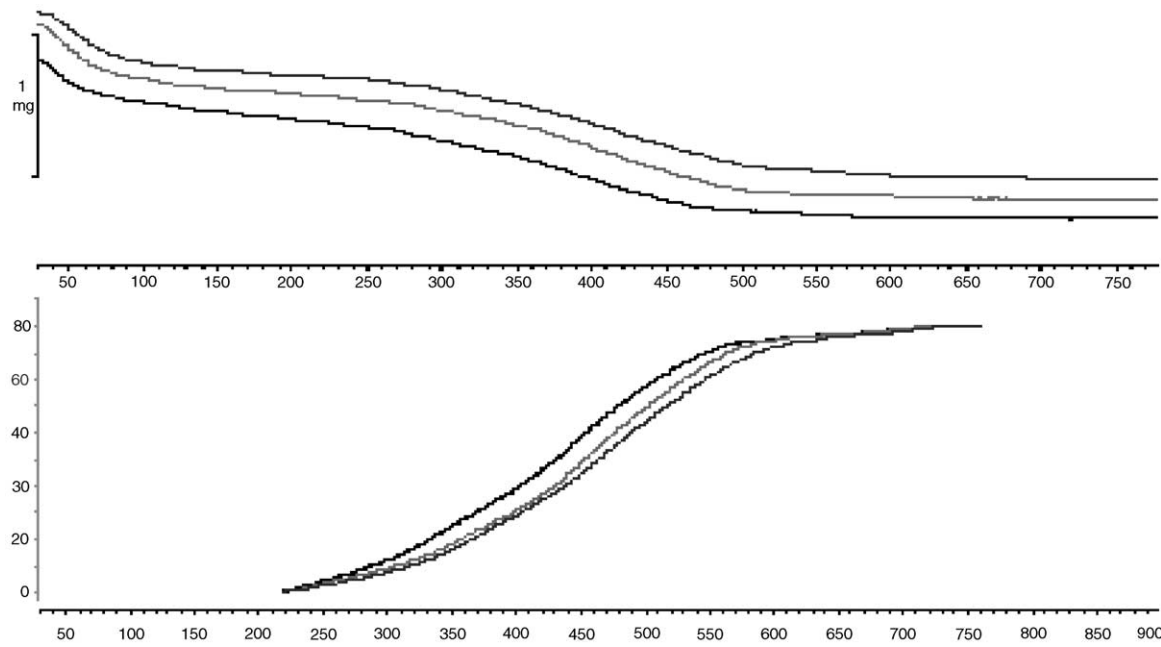


Fig. 3. (a) Multiple heating rate TG curves; (b) conversion versus temperature for coke thermal oxidation in alumina.

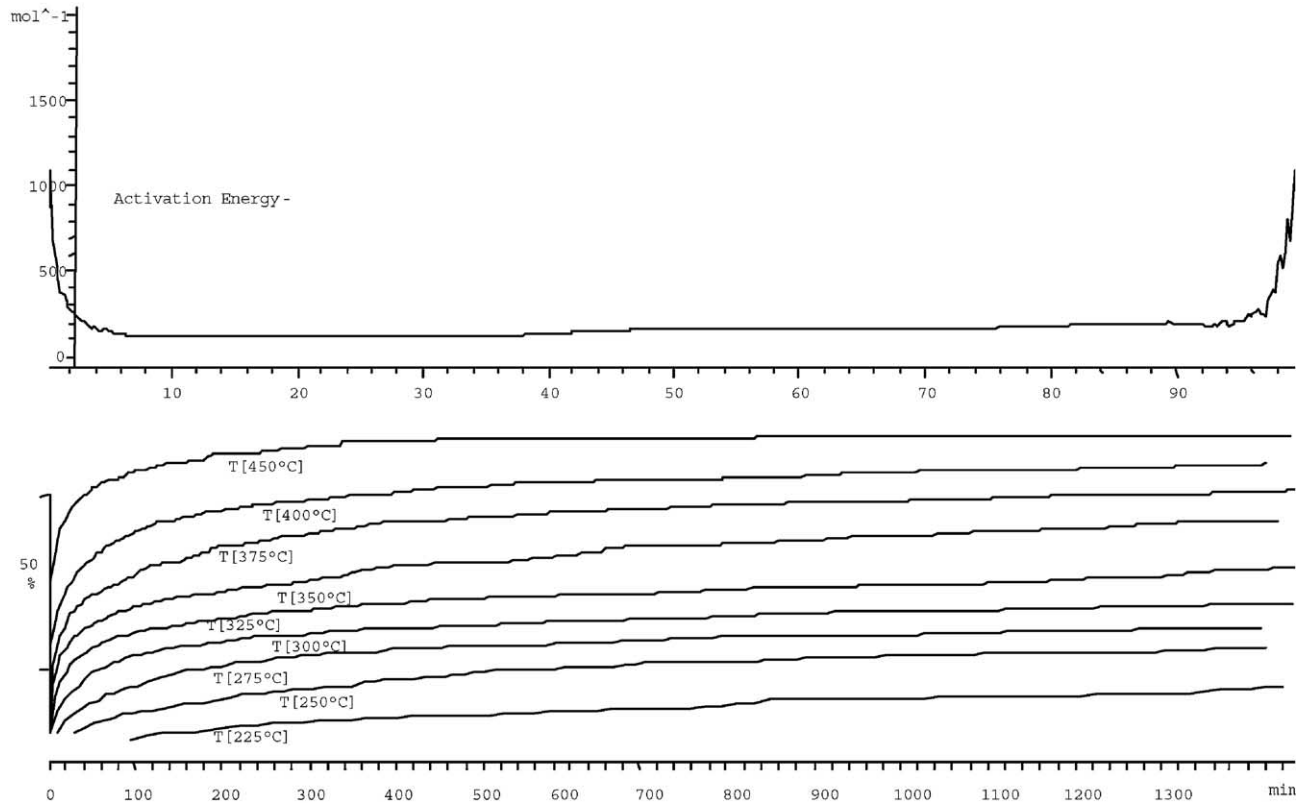


Fig. 4. (a) Activation energy curve and (b) conversion of coke in percentage deposited on alumina versus time for different temperatures.

For example, using a  $\beta$  value of  $10\text{ }^{\circ}\text{C min}^{-1}$ , the thermal oxidation of coke occurs from  $450$  to  $750\text{ }^{\circ}\text{C}$  (Fig. 1).

It can be noted that thermal region of coked 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. Conversion curves as a function of temperature are also showed in Fig. 3.

The activation energy ( $E$ ) was calculated as a function of  $\alpha$  (conversion) and  $T$  (temperature), by using Vyazovkin model-free kinetic method, varying from  $150$  to  $250\text{ kJ mol}^{-1}$  [ $\alpha = 0.1\text{--}0.9$ ] (Fig. 3).

Conversion of coke deposited on alumina as a function of time, for different temperatures, was calculated, noting that the conversion time decreases considerably as a function of temperature (Fig. 4). It was also possible to estimate temperature for removing coke as a function of time, allowing to estimate time required to remove coke for a given temperature (Table 1). It was observed that, to remove 90% of coke from the alumina in a period of 10 h, it would be necessary to carry out thermal oxidation at  $416\text{ }^{\circ}\text{C}$ , with the same purge flow.

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