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MODEL-FREE KINETICS APPLIED TO REGENERATION OF COKED ALUMINA

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Abstract

Thermogravimetry is proposed to study 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 the thermal oxidation of carbonaceous deposits on the catalyst. The activation energy (E) was calculated as a function of α (conversion) and T (temperature), by using Vyazovkin model-free kinetic method, allowing to estimate time required to remove coke at a given temperature.

Keywords: alumina deactivation, catalyst regeneration, model-free kinetics

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 the 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]. The application of thermal analysis for the investigation of catalytic systems and catalysts has been reported in several papers [8, 9]. 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.

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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 MHSV (mass hourly space velocity) of 50 h^{-1}, for 4 h. Under these conditions, the catalysts became 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^{-1}, with a controlled dry air flow of 120 cm^3 min^{-1}. 0.01 g of coked catalyst was used for each experiment.

Results and discussion

The reaction rate of a chemical reaction depends on conversion (α), 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 (α) 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 [10].

Vyazovkin [11, 12] 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. This method has been used for thermal stability evaluation of different systems [13]. The theory is based on that $f(\alpha)$ 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 (β) and the respective conversion curves are calculated out of the TG measured curves.

For each conversion α, $\ln(\beta/T_\alpha^2)$ is plotted *vs*. $1/T_\alpha$, 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 $\beta = dT/dt$:

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

where $\partial\alpha/\partial t$ – reaction rate (s^{-1}), k – rate constant (s^{-1}), α – conversion, β – heating rate ($K\ s^{-1}$).

Substituting k by the Arrhenius expression $k = Ae^{-E/RT}$ and rearranging gives:

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

Integrating up to conversion, α (at the temperature *T*) gives:

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

Since *E*/(*RT*)>>>1, the temperature integral can be approximated by:

$$\int_{\mathrm{T_0}}^{\mathrm{T}}\mathrm{e}^{-\mathrm{E/RT}}\partial T\approx\frac{R}{E}T^2\mathrm{e}^{-\mathrm{E/RT}} \tag{4}$$

Substituting the temperature integral, rearranging and logarithming, gives:

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

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

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

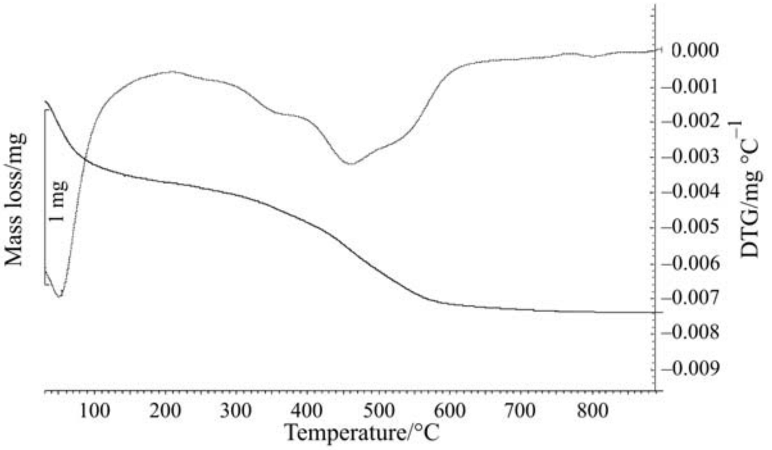

Fig. 1 TG and DTG curves of coked alumina. Heating rate 10 K min^{-1}; dry air flow 120 cm^3 min^{-1}

In order to determine accurately the temperature range of coke thermal oxidation, TG and DTG curves were analysed for each heating rate. For example, using a β value of 10°C min^{-1}, the thermal oxidation of coke occurs from 450 to 750°C (Fig. 1).

It can be noted that the thermal region of coked removal is a direct function of the temperature 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 shown in Fig. 3.

The activation energy (E) was calculated as a function of α (conversion) and T (temperature), by using Vyazovkin model-free kinetic method, varying from 150 to 250 kJ mol^{-1} [α=0.1 to 0.9] (Fig. 4a).

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. 4b). 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°C, with the same purge flow.

Table 1 Temperature (°C) for removing coke as a function of time, for different conversions

Time/min	Conversion/%					
	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	–	–		–	–	

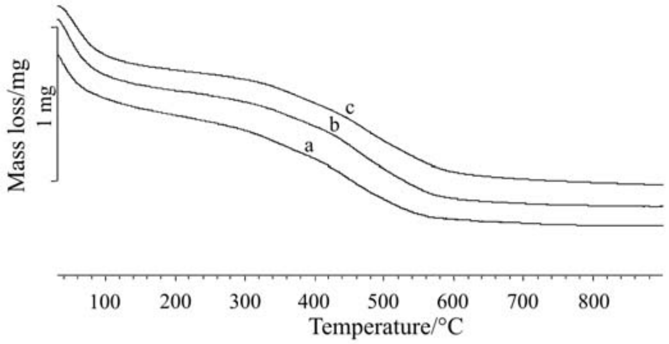

Fig. 2 Multiple heating rate thermogravimetric integral curves for different coke removal rates in % (*w*/*w*). Heating rates: a – 5, b – 10 and c – 20 K min^{-1}

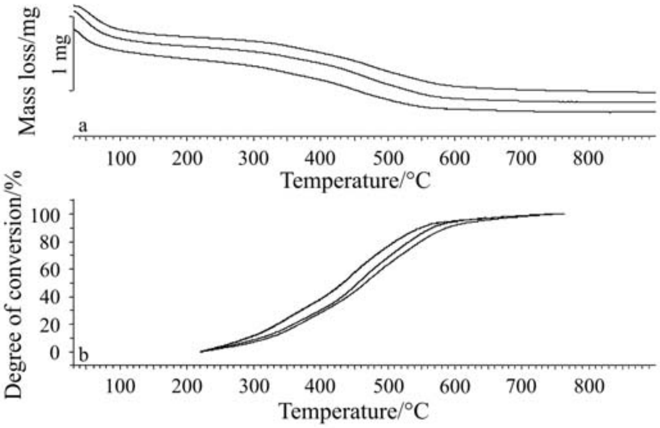

Fig. 3 a – Multiple heating rate TG curves; b – conversion *vs*. temperature for coke thermal oxidation in alumina

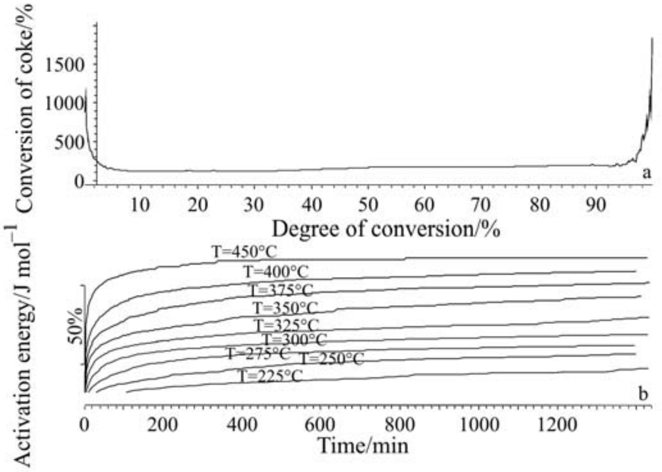

Fig. 4 a – Activation energy curve and b – conversion of coke (in %) deposited on alumina *vs*. time for different temperatures

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