

KINETIC OF REGENERATION OF COKED ALUMINA BY THERMOGRAVIMETRY

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Abstract

Thermogravimetry is used for regeneration of the alumina catalyst which was deactivated by coke, formed in the transformation of 1,3-butadiene in a fixed bed continuous flow reactor. The Vyazovkin model-free kinetic analysis has been applied to data on thermal oxidation of carbonaceous deposits on the catalyst. This analysis has allowed us to estimate the activation energy (E) as a function of α (conversion) and to predict the 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 catalysts is deactivation of a catalyst. Mechanisms of carbon deposition and coke formation on catalysts have been addressed in several reviews [1–4]. Catalysts deactivation occurs primarily as a result of formation of coke [5], which consists of non-reactive polymeric species deposited on the catalyst surface [6]. Catalyst regeneration is generally performed by gradual heating under oxidizing atmosphere [7]. In this work, thermogravimetry is used for studying the kinetics of alumina regeneration. A model-free kinetic analysis is employed to calculate the activation energy and to predict the conversion rates of the coke removal as a function of temperature.

Experimental

The catalyst was synthesized by impregnating aluminum nitrate solution with 25% aqueous ammonium hydroxide. The material was calcined at 823 K under nitrogen flow. The resulting catalyst, which was a solid white powder, was used in the transformation of 1,3-butadiene in a fixed bed continuous flow reactor at 723 K and WHSV (weight hourly space velocity) of 50 h⁻¹, for 4 h. After this period, the catalysts had become deactivated by coking.

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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 10.2 mass% of coke, were submitted to a pre-treatment under a dry air atmosphere at 303 K. They were then heated up to 1173 K at heating rates 5.0, 10 and 20 K min⁻¹, under dry air flow of 120 cm³ min⁻¹. A sample of 0.01 g of coked catalyst was used in each experiment.

Results and discussion

The rate of a chemical reaction depends on conversion (α), temperature (T) and time (t). A function of conversion $f(\alpha)$ is different for specific reaction mechanism and needs to be determined experimentally. For simple-step reactions, one can evaluate $f(\alpha)$ in terms of the well known reaction models. For multi-steps reactions the conversion dependence of the reaction rate is much more complex, so the use of single-steps models results in unreasonable kinetic data. In this situation, a trustworthy way of obtaining reliable and consistent kinetic information is to employ model-free kinetic analysis [8].

Vyazovkin *et al.* [9, 10] developed an integral method of model-free kinetic analysis which as multiple heating rates and allows one to evaluate both simple and complex reaction kinetics. The analysis is based on the isoconversional principle which states that at a constant conversion the reaction rate is only a function of temperature. In order to employ this method an experiment has to be carried out at least at three different heating rates (β) and the respective conversion curves are evaluated from the measured TG curves. For each conversion α , $\ln(\beta/T_\alpha^2)$ 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.

The basic equation of non-isothermal kinetics is as follows

$$\frac{d\alpha}{dT} = \frac{k}{\beta} f(\alpha) \quad (1)$$

where k is the rate constant (s⁻¹), β : heating rate (K s⁻¹). Replacing k with the Arrhenius expression $k=k_0e^{-E/RT}$ and rearranging gives:

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

Integrating of the Eq. (2), gives:

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

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

$$\int_0^T e^{-E/RT} dT \approx \frac{R}{E} T^2 e^{-E/RT} \tag{4}$$

Substituting the temperature integral, rearranging and logarithming, gives:

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

where the subscript α denotes values related to a given extent of conversion.

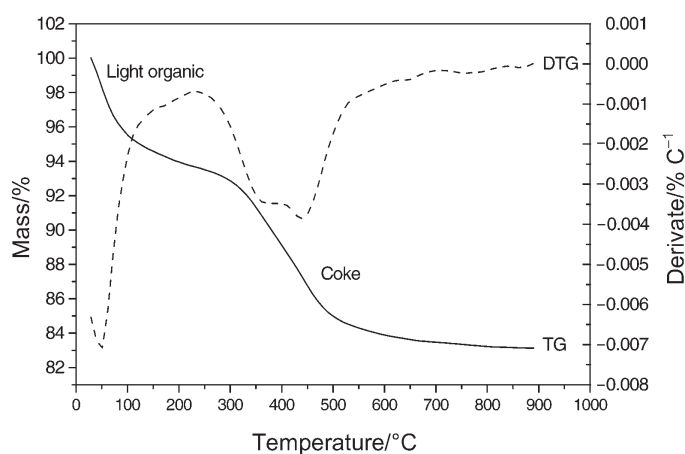


Fig. 1 Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of coked alumina. Heating rate 10 K min⁻¹; dry air flow 120 cm³ min⁻¹

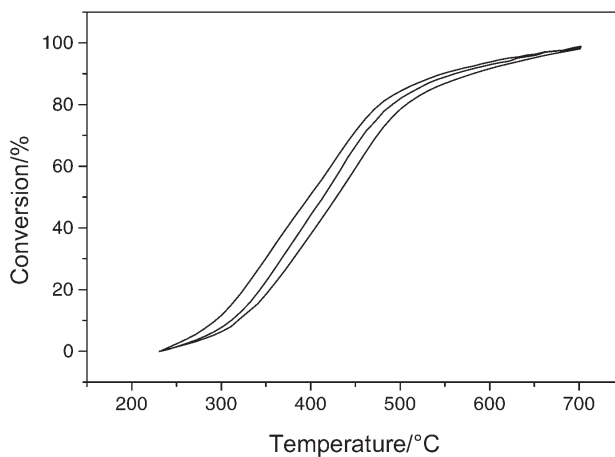


Fig. 2 Multiple heating rate thermogravimetric integral curves for different coke removal rates in % (mass/mass). From left to right: 5.0, 10 and 20 K min⁻¹

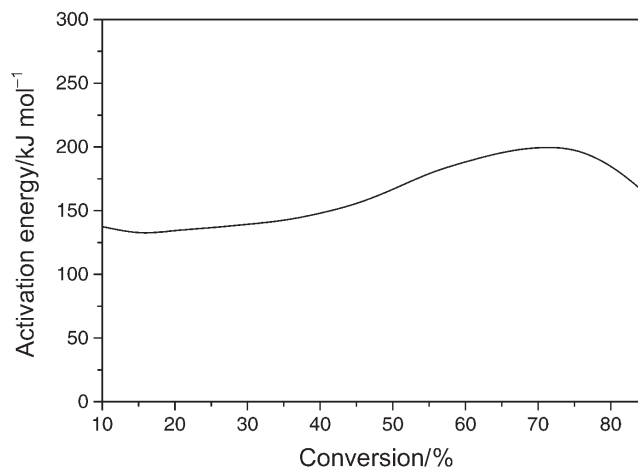


Fig. 3 Activation energy vs. conversion for coke thermal oxidation in alumina

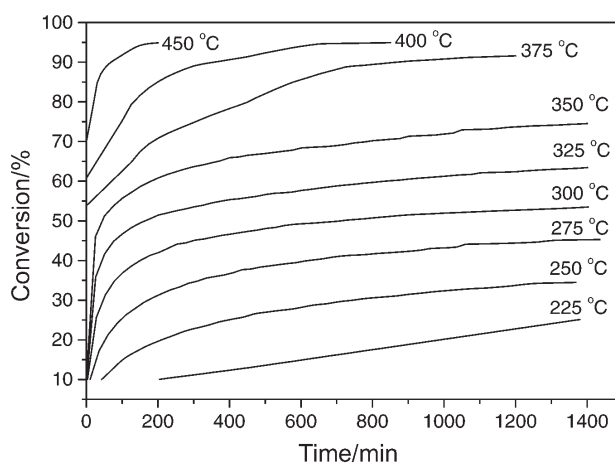


Fig. 4 Conversion of coke (in %) deposited on alumina vs. time for predicted temperatures

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 303 to 503 K, is due to desorption of 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. For example, at 10 K min^{-1} the thermo-oxidation of coke occurs from 503 to 1023 K (Fig. 1).

It should be noted that the temperature region of coke removal depends on the temperature gradient in the samples and is 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.

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

K	10%	25%	50%	75%	90%	95%
2 h	506	543	604	664	705	–
4 h	495	531	592	652	685	717
6 h	389	524	585	645	672	703
8 h	385	519	580	640	663	692
10 h	382	516	576	639	657	685
12 h	379	513	573	636	652	679
14 h	377	510	571	633	648	674
16 h	375	508	569	631	645	669
18 h	373	506	567	629	642	665
20 h	–	505	565	628	639	662
22 h	–	503	563	626	637	659
24 h	–	–	–	–	–	–

By using Vyazovkin's model-free kinetic method, we found from 135 to 185 kJ mol⁻¹ (Fig. 3). The conversion dependence of the activation energy was further used to predict the conversion of coke for different temperatures by using a model-free algorithm [9, 10]. The conversion time decreases markedly with temperature (Fig. 4). We also estimated the time required to remove coke to a certain extent at 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 657 K, with the same purge flow.

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References

- 1 J. Haber, J. H. Block and B. Delmon, *Pure Appl. Chem.*, 67 (1995) 1257.
- 2 C. N. Satterfield, in: *Heterogeneous Catalysis in Industrial Practice*, McGraw-Hill, New York.
- 3 C. H. Bartholomew, *Chem. Eng.*, 12 (1984) 97.
- 4 E. B. Maxted, *Adv. Catal.*, 3 (1951) 129.
- 5 R. Hughes, *Deactivation of Catalysts*, Academic Press, London 1984, p. 3.
- 6 P. Magnoux, M. Guisnet, S. Mignard and P. Cartraud, *J. Catal.*, 117 (1989) 495.
- 7 P. G. Menon, *J. Mol. Catal.*, 59 (1990) 207.
- 8 S. Vyazovkin and C. A. Wight, *Thermochim. Acta*, 340-341 (1999) 53.
- 9 S. Vyazovkin and V. Goryachko, *Thermochim. Acta*, 194 (1992) 221.
- 10 S. Vyazovkin and A. I. Lesnikovich, *Russ. J. Phys. Chem.*, 62 (1988) 2949.