KINETIC STUDIES OF OXIDATION OF RESIDUAL CARBON FROM MOROCCAN OIL SHALE KEROGENS

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Residual carbons from kerogen extracted from two Moroccan oil shales (from Timahdit and Tarfaya) were oxidized in air. The oxidations were studied by isothermal thermogravimetry. Several kinetic models for mechanisms of the reactions were tested to fit the experimental data. Oxidation of the residual carbon derived from Timahdit oil shale followed a two-third order reaction with an activation energy of 58.5 kJ mol^{-1}, whilst that from Tarfaya oil shale was a half order reaction with activation energy of 64.1 kJ mol^{-1}.

Keywords: isothermal thermogravimetry, kerogen, kinetics, oil shale, residual carbon, Tarfaya, Timahdit

Introduction

We have previously made extensive studies on the reactivity of Moroccan oil shales [1–8].

Kinetic studies on the oxidation of Timahdit and Tarfaya oil shales by TG and DTA showed that there were two well-defined stages in the reaction [6]. Activation energies were determined by the Kissinger and by the Coats–Redfern methods, and gave a value of 103 kJ mol^{-1} for the first stage of both oil shales. However, for the second stage (at higher temperatures), the activation energies were 148 and 118 kJ mol^{-1} for the Timahdit and Tarfaya shales, respectively.

The pyrolysis of Timahdit and Tarfaya oil shales in a nitrogen atmosphere, leading to the removal of volatile matter and formation of residual carbon, has been studied also by TG and DTA for temperatures up to 500°C [7]. Again two stages of reaction were observed with activation energies of 41.3 and 41.5 kJ mol^{-1} for the Timahdit and Tarfaya shales at the lower temperature stage and 64.3 and 61.3 kJ mol^{-1} at the higher temperature stage, respectively. Oxidation of the residual carbons, obtained at 500°C, was studied by isothermal TG at this temperature. The oxidation was shown to obey first order kinetics.

The reaction with carbon dioxide of residual carbon, obtained from kerogen extracted from the two oil shales, was studied by TG and DTA [8]. Activation energies were determined for different heating rates by the methods of Kissinger, Coats–Redfern and Chen–Nuttall. Two stages of reaction were observed.

In this paper, we describe the oxidation in air of residual carbon from kerogen, extracted from the two Moroccan oil shales, studied by isothermal thermogravimetry in the temperature range 340–500°C.

The general characteristics of the two oil shales were reported in our earlier work [7], as were the elemental compositions of their kerogens and their residual carbons [8].

Experimental

The kerogen samples were obtained by leaching the raw oil shales with a mixture of hydrochloric and hydrofluoric acids. The residual carbons were prepared by heating the kerogen samples in flowing nitrogen (gas flow rate 35 cm^3 min^{-1}, heating rate 12°C min^{-1}) until a temperature of 500°C was reached, and maintaining the product at this temperature for 1 h to eliminate all volatile matter.

Isothermal TG was carried out on a Stanton-Redcroft STA780 thermal analyser at a series of preset temperatures ranging from 340 to 500°C in flowing air (gas flow rate 35 cm^3 min^{-1}).

Figures 1 and 2 show the isothermal TG curves for the residual carbons from kerogens of the two oil shales; the extent of reaction (expressed as a fraction of the initial mass of reactant), α, is plotted as a function of time.

Results and discussion

It is first necessary to establish that each of the residual carbons undergo oxidation by the same mechanism in the respective temperature ranges of the isothermal TG
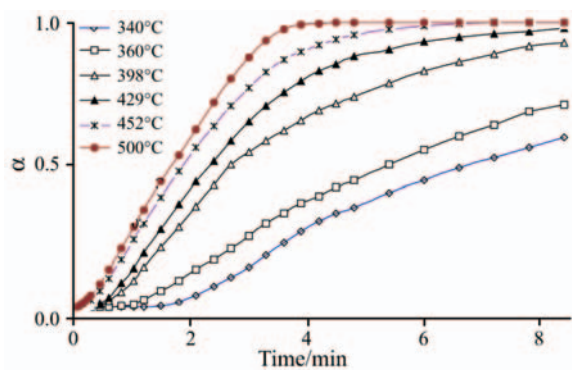
Fig. 1 Extent of reaction *vs*. time for oxidation of residual carbon from kerogen derived from Timahdit oil shale

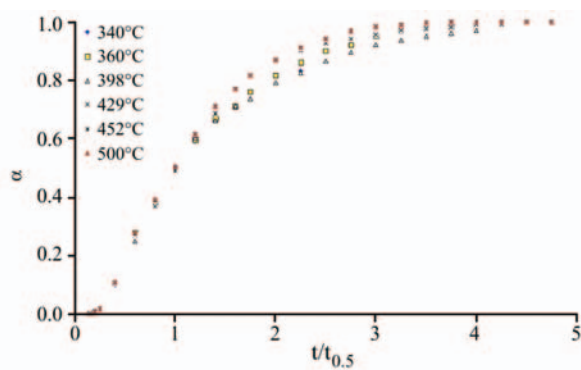**Fig. 3** Plot of α *vs*. $t/t_{0.5}$ for residual carbon from kerogen derived from Timahdit oil shale

Fig. 2 Extent of reaction *vs*. time for oxidation of residual carbon from kerogen derived from Tarfaya oil shale
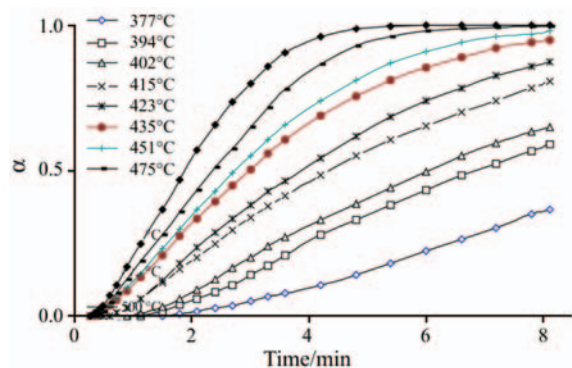
Fig. 4 Plot of α *vs*. $t/t_{0.5}$ for residual carbon from kerogen derived from Tarfaya oil shale

studies. The method described by Sharp *et al*. [9] and reported by Delmon [10] was used for this. Here the extent of reaction, α, is plotted as a function of time, where the time is expressed as a fraction (or multiple) of the time for an arbitrary fraction of the initial amount of the material to undergo reaction. The arbitrary fraction is often taken as half; thus, the time is expressed as a fraction (or multiple) of $t_{0.5}$, where $t_{0.5}$ is the time when $\alpha=0.5$ in the isothermal TG curves. Figures 3 and 4 show plots of α *vs*. $t/t_{0.5}$, for the isothermal data in Figs 1 and 2, respectively. It is seen that the data for all the temperatures fit into the same curve for values of α up to 0.75, confirming that the mechanism of the oxidation reaction for each of the residual carbons is unchanged in the temperature ranges of the TG curves.

Three kinetic models reported by Delmon [10] were examined for fitting in the experimental data. In all cases the rate was assumed to be first order with respect to the partial pressure of oxygen, $p(O_2)$, in accordance with literature data [11–13]. This parameter was constant, because the oxidations were carried out under a constant flow rate of air.

First order kinetics with respect to the amount of residual carbon would give the equation:

$$-\ln(1-\alpha)=kp(O_2)t \qquad (1)$$
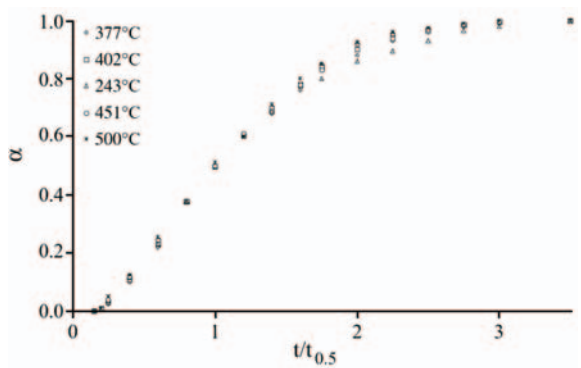
For needle-shaped particles reacting by an advancing interface mechanism, the rate equation is of half order, and the integrated form is:

$$1-(1-\alpha)^{1/2}=kp(O_2)t \qquad (2)$$

For spherical particles reacting by an advancing interface mechanism, the corresponding form of the rate equation is of two-third order:

$$1-(1-\alpha)^{1/3}=kp(O_2)t \qquad (3)$$

At constant partial pressure of oxygen, the above equations reduce to, respectively:
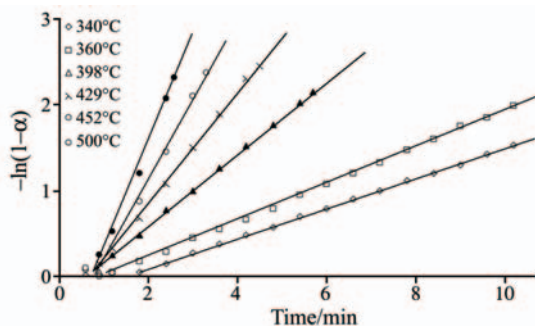
$$1-(1-\alpha)^{1/2}=k't \qquad (1')$$

$$1-(1-\alpha)^{1/2}=k't \qquad (2')$$
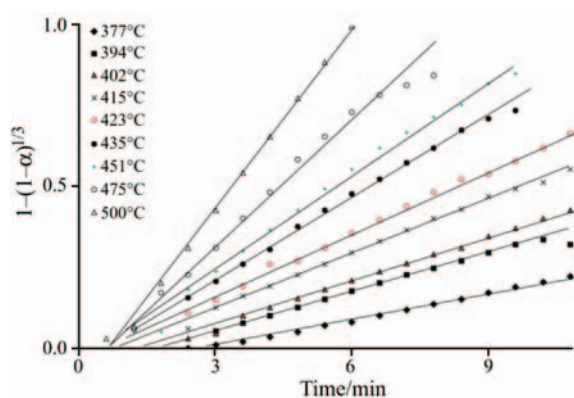
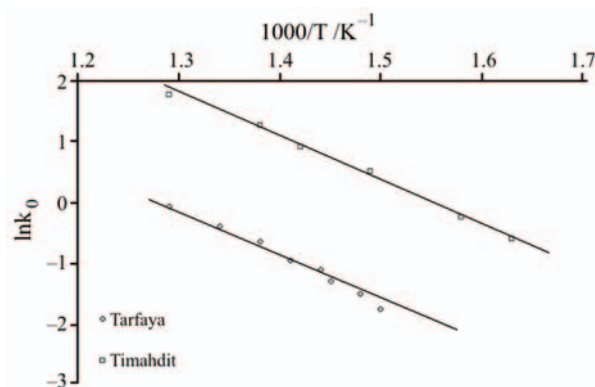$$1-(1-\alpha)^{1/3}=k't \qquad (3')$$

where

$$k'=kp(O_2)$$

Analysis of the experimental results showed that the air oxidation of residual carbon from kerogen extracted from Timahdit oil shale fitted Eq. (3'), as shown in Fig. 5. For the residual carbon of kerogen derived from Tarfaya shale, the experimental data fitted Eq. (1'), Fig. 6. Arrhenius plots are shown in

Fig. 5 Plot of $-\ln(1-\alpha)$ *vs.* time for the isothermal oxidations of residual carbons from kerogen derived from Timahdit oil shale

Fig. 6 Plot of $1-(1-\alpha)^{1/3}$ *vs.* time for the isothermal oxidations of residual carbons from kerogen derived from Tarfaya oil shale

Fig. 7 Arrhenius plots for oxidations of residual carbons from kerogens derived from Timahdit and Tarfaya oil shales

Fig. 7, from which the activation energy of oxidation of residual carbon derived from kerogen extracted from Timahdit oil shale is calculated as 58.5 kJ mol^{-1}. The corresponding figure for the carbon obtained from Tarfaya shale is 64.1 kJ mol^{-1}.

Conclusions

Isothermal TG studies on oxidation of residual carbon from kerogen extracted from two Moroccan oil shales showed that the oxidation of the carbon derived from Timahdit shale obeyed a two-third order law, in accordance with an advancing interface mechanism for spherical particles. For the carbon from Tarfaya oil shale, the order of reaction is half, fitting into a kinetic model for surface reaction of needle-shaped particles.

Acknowledgements

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