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Thermal decomposition of adsorbed β-carotene and chlorophyll on acid-activated clay

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Abstract

β-Carotene and chlorophyll have been adsorbed from solution in benzene and hexane onto acid-activated clay. Five steps were observed during the thermal decomposition of β-carotene and chlorophyll on acid-activated clays. The adsorbed solvents desorbed during the first step and the adsorbed materials decomposed during the dehydroxylation of the clay. The activation energies of all the steps have been determined.

INTRODUCTION

Acid-activated clays are widely used in the vegetable-oil industry [1,2]; the clay (0.15–3.00%) is used as a decolorizing agent [3]. These clays, after filtration, can be regenerated to almost their original activity and can be reused a number of times. The regeneration of the clay depends on a large number of factors, such as the price of the raw clay, the cost of regeneration and the fall in efficiency.

The regeneration of the clay involves two main steps: recovery of the retained or entrapped oil and removal of adsorbed coloring matter such as carotenoids, xanthophylls, lycopene, chlorophylls, tocopherols and gassypol [4,5].

After removal of retained or entrapped oil, the final regeneration step [6], i.e. the removal of adsorbed coloring materials, may be achieved by burning [7] or extraction with solvents [8–10].

The kinetic parameters of the decomposition of coloring materials on acid-activated clays are quite important for regeneration of the clays under controlled temperatures. In the present study, the decomposition of adsorbed β-carotene and chlorophyll on acid-activated clay was studied using DTA and TG measurements in order to clarify the regeneration of clays after decolorizing of the oils.

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As reported previously [11], the determination of the kinetic parameters using the following equation, i.e. by plotting $\ln[-\ln(1-\alpha)/T^2]$ against $1/T$, seems to give results that are more accurate than those obtained from the well-known Coats–Redfern equation

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}$$

EXPERIMENTAL

The adsorption of β-carotene [12,13] and chlorophyll [14] on acid-activated clay has been described previously.

DTA and TG traces were obtained on a Netzsch DTA–TG simultaneous instrument at a heating rate of 10 K min^{-1} in argon and static atmosphere, using kaolin heated to 1200°C as inert material.

RESULTS AND DISCUSSION

β-Carotene and chlorophyll were adsorbed on acid-activated clay from solution in benzene and hexane. DTA and TG curves of these dried samples are shown in Figs. 1–3.

There is a complex endothermic peak due to desorption of organic solvent (benzene and hexane) and dehydration of water at 105°C, the event being complete at about 160°C. The weight loss in this period is about 4% and 5% for the β-carotene and chlorophyll adsorbed samples, respectively.

The values of $\ln[-\ln(1-\alpha)/T^2]$ were then plotted against $1/T$ for three samples (Fig. 4).

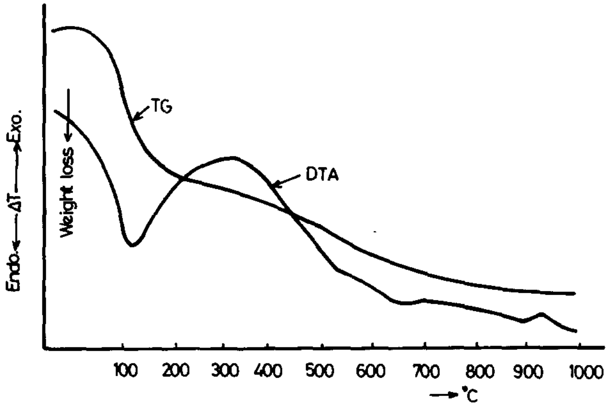

Fig. 1. DTA and TG curves of activated clay after β-carotene adsorption (in static atmosphere).

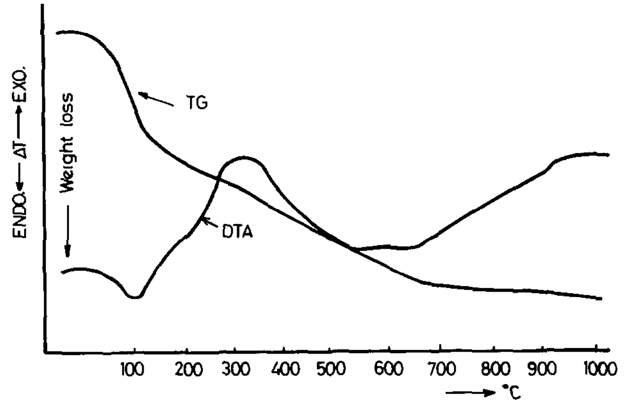

Fig. 2. DTA and TG curves of activated clay after chlorophyll adsorption (in static atmosphere).

The activation energies are shown in Table 1. The activation energies of dehydration of hygroscopic moisture are very similar in the static atmosphere. Hexane is desorbed more easily in a static atmosphere than in an inert atmosphere.

The activation energies of decomposition of adsorbed β-carotene and chlorophyll on acid-activated clay in the static atmosphere are −5.03 and −3.13 kJ mol^{-1}, respectively.

The adsorbed clay shows a continuous weight loss from about 150 to 1000°C.

β-Carotene decomposes more easily than chlorophyll in argon atmosphere above 550°C. Carbonaceous material is oxidised more easily in the static atmosphere than in the inert atmosphere. In argon atmosphere,

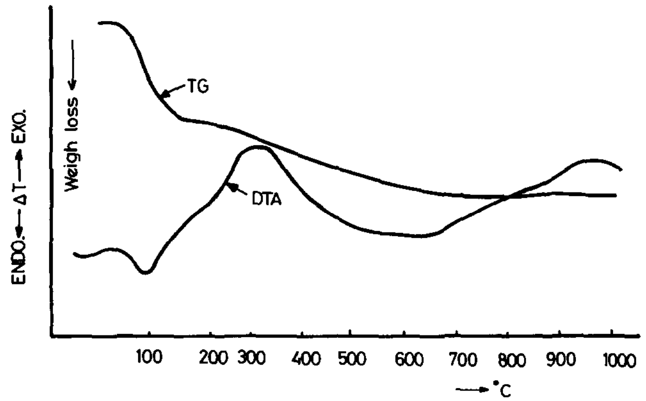

Fig. 3. DTA and TG curves of activated clay after chlorophyll adsorption (in argon atmosphere).

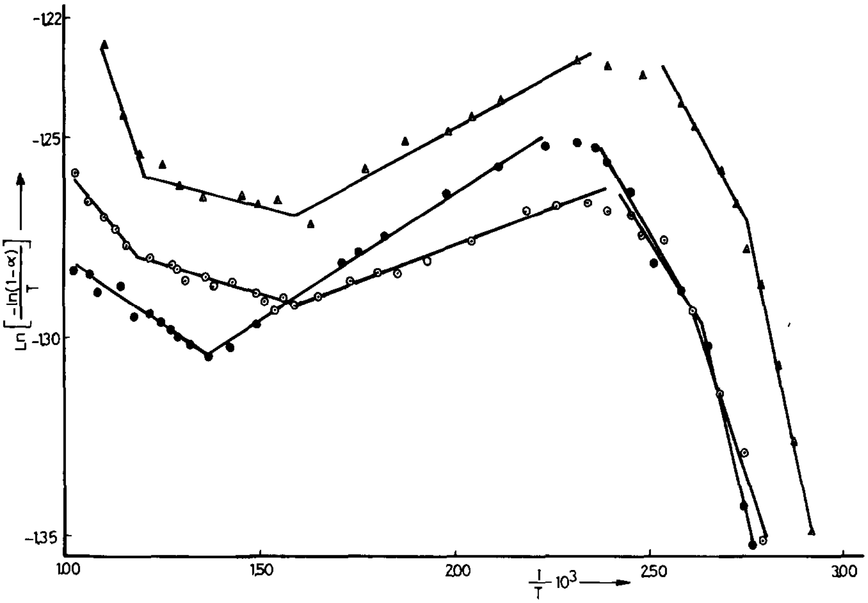

Fig. 4. Plots of $\ln[-\ln(1-\alpha)/T^2]$ against $1/T$: ●, β-carotene (static atmosphere); ○, chlorophyll (static atmosphere); △, chlorophyll (argon atmosphere).

TABLE 1

Activation energies of decomposition of β-carotene and chlorophyll on acid-activated clay

	Temperature range (°C)	Activation energy (kJ mol^{-1})	Correlation cofficient	Reaction
β-Carotene (in static atmosphere)	< 110	31.44	−1.00	Desorption of benzene
	110–160	13.09	−0.98	Dehydration
	160–465	−5.03	1.00	Combustion
	465–550	5.49	−0.96	Combustion and dehydroxylation
	> 550	5.49	−0.96	Dehydroxylation
Chlorophyll (in static atmosphere)	< 110	30.95	−0.97	Desorption of hexane
	110–160	9.02	−0.97	Dehydration
	160–330	−3.13	0.99	Combustion
	330–550	2.55	−0.93	Combustion and dehydroxylation
	> 550	11.63	−1.00	Dehydroxylation
Chlorophyll (in argon atmosphere)	< 90	35.91	−0.99	Desorption of hexane
	90–145	14.50	−1.00	Dehydration
	145–340	−3.80	0.99	Combustion
	340–550	1.06	−0.73	Combustion and dehydroxylation
	> 550	26.10	−0.99	Dehydroxylation

therefore, chlorophyll-adsorbed clay has a much higher activation energy than in the static atmosphere.

These results will be of value in further investigations into the regeneration of clays.

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