

DECOMPOSITION KINETIC OF A SYNTHETIC OIL ADSORBED ON DIFFERENT SILICO-ALUMINA

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The thermooxidative degradation of three models of oily soils was studied under non-isothermal conditions, at heating rates of 5, 10, 15 and 20°C min⁻¹. Di-octyl-sebacate, as model for synthetic oil, was adsorbed on silica, alumina and silico-alumina, considered models for the inorganic micelle of a soil. For a kinetic analysis, the TG data were processed by three methods: Flynn–Wall–Ozawa, Friedman and NPK (Nomen–Sempere). The results indicate the NPK as the less speculative method that allows a separation of the elementary steps and at the same time a separation of the temperature, respective conversion dependent part of the reaction rate.

Keywords: artificial oily soil, model soil, non-isothermal kinetics

Introduction

A strong demand for oil products has created significant environmental problems. For many years, discharge of various oil-bearings wastes and accidental spills of oil on land and in water streams have contaminated billion of tons of soil and sediment [1].

On the kinetic of oil oxidation also with catalytic effect of additives, some recent papers were reported [2, 3].

But in the field of oily wastes the most part of the earlier works deals with the sample characterization under isothermal and/or non-isothermal conditions [4, 5]. The trend evidenced at the 13th ICTAC Congress [6] was the modeling of sample/material behavior in dynamic conditions and therefore the kinetic studies should be performed on chemical well-characterized samples.

In our previous work [5] the main difficulty was due to the soil sample (a chernozem). Its inhomogeneity and the intrinsic complex composition of the soil led to a rather speculative interpretation of the obtained data.

The aim of the present work is to perform a kinetic study under non-isothermal conditions of the thermal degradation of an artificial polluted model soil. For modeling the inorganic micelle of the soil, essentially a silico-alumina, we used a silica, an alumina and a silico-alumina gel. As model for the oily pollutant, di-octyl sebacate (DOS) was used.

Experimental

Materials

- SO Silica, reagent grade, REAHIM, St. Petersburg, Russia
AO Alumina, catalyst support, M. WOELM, Eschwege, Germany
SAO Silico-alumina gel, chromatography, CHEMAPOL, Praha, Czech Republic

The oil model DOS was a base grade synthetic oil.

The samples were prepared by impregnation of the solid with oil, followed by trickling out the excess oil. The mass of oil adsorbed is determined directly from the TG curves.

Thermogravimetric analysis

The experimental data were obtained on a Perkin-Elmer DIAMOND TG/DTG device, under dynamic air atmosphere (100 mL min⁻¹), using Al crucibles and heating rates, β , of 5, 10, 15 and 20°C min⁻¹, in the range 50–500°C.

Results and discussion

In Fig. 1, three typical curves are presented.

In all three cases, the curves are well-defined and the data are easy to interpret:

- the thermal degradation is due an oxidation process (see the heat flow curves);
- by samples DOS/SO and DOS/SAO, the maximum of reaction rate (DTG) coincide with the maximum

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of the heat flow; the exception by DOS/AO samples is certainly due a catalytic effect of alumina. An argument for this is the maximum of DTG at 220°C for DOS/AO, instead of 240–260°C for the other two samples

- the mass loss, Δm , (mass%), i.e. the quantity of DOS adsorbed, was:

DOS/SO	11.3%
DOS/AO	12.9%
DOS/SAO	9.9%

Kinetic analysis

At beginning, the TG data were processed by the isoconversional method of Flynn–Wall [7] and Ozawa [8]. Using the equation

$$\ln \beta = \ln \left[A \frac{f(\alpha)}{d\alpha/dT} \right]_{\alpha} - \frac{E}{RT} \quad (1)$$

values of the activation energy corresponding to different conversion degrees were obtained. The data are presented in Table 1.

The only acceptable dispersion of the E values is that by oily silico-alumina. But generally, in the range of $\alpha=0.3-0.6$, the values of E are narrow enough for a first approximation: by silica and silico-alumina, the mean E values are the same, while by alumina, where the E value is lower with 10–15 kJ mol⁻¹, a catalytic effect is obvious.

For comparison, the kinetic analysis was continued with the differential-isoconversional method by Friedman [9].

From the generally accepted equation of the non-isothermal kinetics:

$$\beta \frac{d\alpha}{dT} = f(\alpha) A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where α is the degree of conversion, β is the heating rate and T is the temperature in K; the equation corre-

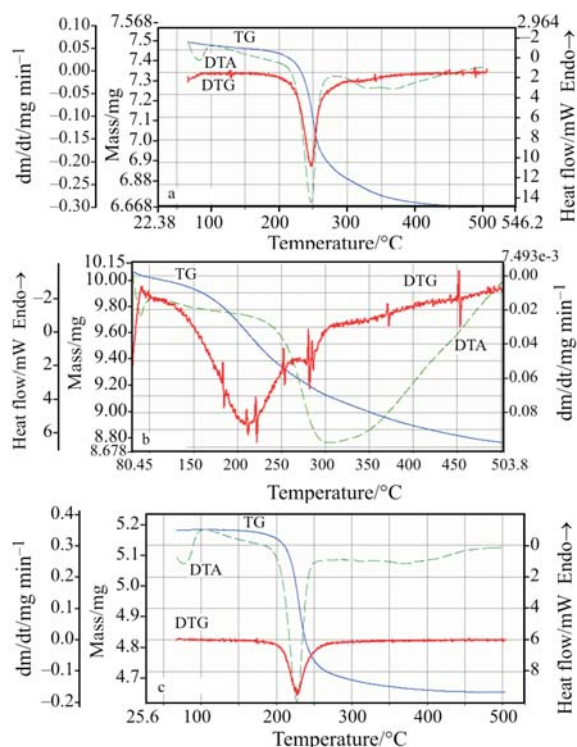


Fig. 1 Thermoanalytical curves at 10°C min⁻¹ for: a – DOS/SO, b – DOS/AO and c – DOS/SAO

sponding to the Friedman's differential isoconversional method, was obtained:

$$\ln \left(\beta \frac{d\alpha}{dT} \right) = \ln [A f(\alpha)] - \frac{E}{RT} \quad (3)$$

For $\alpha=\text{const.}$ and using various heating rates, the plot $\ln[\beta(d\alpha/dT)]$ vs. $1/T$ should be linear. From the slope and the intercept of the straight line the value of activation energy (E) and product $[A f(\alpha)]$ were obtained.

The values of the activation energy are presented in Table 2.

There is an obvious variation of E vs. α , but this is not monotonous, for a conversion function $f(\alpha)$ will have been tested. By alumina and silico-alumina, the

Table 1 The activation energy vs. conversion by FWO method

Sample	Activation energy/kJ mol ⁻¹ for $\alpha=$									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	main
DOS/SAO	74.1	72.1	72.2	73.5	74.0	74.4	75.4	75.3	74.7	74.0
DOS/SO	85.5	75.8	75.0	75.3	75.0	73.3	70.9	66.3	59.6	73.0
DOS/AO	51.7	54.0	57.7	59.5	58.0	63.1	64.1	66.1	67.5	60.2

Table 2 The dependence on conversion of the activation energy by Friedman's method

Sample	Activation energy/kJ mol ⁻¹ for $\alpha=$									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	main
DOS/SAO	63.9	65.4	72.3	76.2	75.7	73.9	70.4	68.7	79.1	71.7
DOS/SO	63.3	67.2	64.6	69.6	62.2	53.7	47.4	35.3	34.0	55.2
DOS/AO	71.3	54.5	60.7	61.3	60.0	60.9	58.6	70.5	70.9	63.2

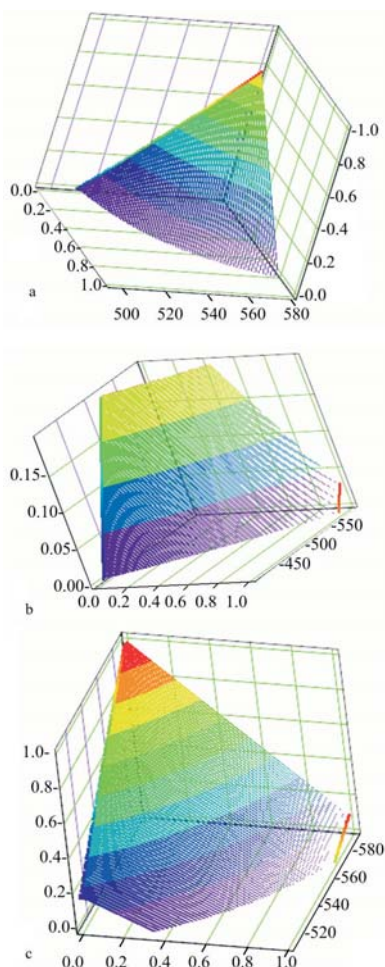


Fig. 2 The reaction rate surfaces for a – DOS/SO, b – DOS/AO and c – DOS/SAO

main values obtained by FWO, respective Friedman's method are in a good agreement.

Due to the above mentioned uncertainty, we appealed to the non-parametric kinetic method [10–16].

By this method it is accepted that the reaction rate can be expressed as a product of two separable functions:

$$r_{ij}=f(T_j)g(\alpha_i) \quad (4)$$

Consequently, the experimental points obtained by different heating rates β , can be expressed in a 3D space, with the coordinates of (T_j, α_i, r_{ij}) .

These points are interpolated by a proper algorithm and a continuous surface of the reaction rate (according to Eq. (4)) is obtained (Fig. 2).

Also as a consequence of Eq. (4), this surface can be suitable discretized into an $i \times j$ square matrix:

$$M=\{r_{ij}\} \quad (5)$$

The columns account for the temperature T_j and the rows refer to conversion degree α_i , so that the Eq. (5) can be rewritten as:

$$M=\{g(\alpha_i)f(T_j)\} \quad (6)$$

The NPK method uses the singular value decomposition (SVD) algorithm [17] to decompose the matrix M:

$$M=U(\text{diag } s)V^T \quad (7)$$

In this way the influence of the conversion respective temperature are separated since:

- a vector u_1 given by the first column of the matrix U is analyzed vs. α to determine the conversion function $g(\alpha)$; we suggest the Šesták–Berggren equation [18]:

$$g(\alpha)=\alpha^m(1-\alpha)^n \quad (8)$$

- a vector v_1 given by the first column of the matrix V is searched for the temperature dependence $f(T)$; a classical Arrhenius equation was suggested.

Also the SVD algorithm allows separating two or more simultaneous steps of a complex process.

Indeed, if the observed reaction rate at α_i and T_j is:

$$r_{ij}=r_1(ij)+r_2(ij)=g_1(\alpha_i)f_1(T_j)+g_2(\alpha_i)f_2(T_j) \quad (9)$$

the corresponding matrix M became:

$$M=U_1(\text{diag } s_1)V_1^T+U_2(\text{diag } s_2)V_2^T \quad (10)$$

and so two independent vectors u_1 and u_2 for simulating the conversion function, respectively two independent vectors v_1 and v_2 for temperature dependence should be obtained.

The contribution of each step to the total process is quantitatively expressed by the explained variance, λ_i , so that $\sum \lambda_i=100\%$.

The obtained kinetic parameters are systematized in Table 3.

Remarkable by this method are the two separation abilities:

- between the temperatures, respective the conversion dependent part of the reaction rate

Table 3 The kinetic parameters according to NPK method

Sample	λ	$E/\text{kJ mol}^{-1}$	A/min^{-1}	m	n	$\bar{E}=\sum(\lambda E)$
DOS/SAO	90.7	45.6	$1.072 \cdot 10^4$	1	2	49.4
	9.2	87.7	$2.509 \cdot 10^8$	1	3/2	
DOS/SO	92.6	44.7	$5.959 \cdot 10^3$	2/3	2	45.3
	7.1	54.8	$5.476 \cdot 10^7$	1	1	
DOS/AO	73.4	76.0	$2.109 \cdot 10^7$	2	0	64.4
	26.6	32.4	$1.048 \cdot 10^3$	0	1/3	

- between one or two elementary steps of a complex process

In a good agreement with the graphical representation, the oxidative degradation of the adsorbed DOS takes place by one step in the case of silica and silico-alumina (contribution of $\lambda < 10\%$ can be neglected). By alumina, there are clearly two steps; this is indicated also in Fig. 1b by a larger DTG and HF peaks.

Regarding to the values of the activation energy, by alumina, the mean value ($\bar{E} = \Sigma(\lambda E)$) is in a very good agreement with these of FWO and Friedman's methods.

Conclusions

The thermooxidative decomposition of an adsorbed DOS depends on the nature of the support. Because the utilized support simulates the inorganic component of a soil, the origin of the soil will influence its thermal behavior. High alumina content in the inorganic micelle will have a catalytic effect.

An apparent simply process on the TG curves is in reality enough difficult to be studied from the kinetics point of view. Just in one case, on alumina, the values of the activation energy are narrow. However, the NPK method allows a less speculative separation between the influence of temperature and conversion, respectively a separation of a complex process into its elementary steps.

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