RE-EXAMINATION OF THE KINETICS OF THE THERMAL DEHYDROXYLATION OF GOETHITE

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Abstract

The kinetics of thermal dehydroxylation of aluminuous goethites [1] synthesised from a ferrous salt has been re-examined using the general reaction order kinetic law. The utilised data processing was based on the procedures employed by dissolution kinetics. Recalculation of the activation energies E_A of the dehydroxylation yielded the values 130, 132, 128, and 123 kJ mol^{-1} for pure goethite, goethite with 10, 20, and 30 mol% Al substitution, respectively. The values of E_A are in a good agreement with those given for goethite in literature. The E_A values are linearly related with the chemically bound excess H_2O/OH^- in the crystal lattice that is apparently influenced by Al substitution.

Introduction

Calculations of kinetic characteristics, namely the pre-exponential factor, activation energy, and dissolution rate coefficients from experimentally obtained thermogravimetric or dissolution curves require choosing a correct kinetic law [2]. However, all kinetic laws employed for data processing are based on simplified, one-sided assumptions, stressing influence of just the particle geometry (the general reaction order law, GRO) or just the nucleation kinetics (Kabai or JMAYK equations) as if only one of these models was exactly valid in each particular case. On the contrary, both dissolution and thermal dehydroxylation of goethite [3, 4] were described using either the GRO or Kabai equations but no explanation has been given why the same reactions of the same phase is controlled

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by different kinetic laws. According to Koga *et al.* [3] the number of hematite nuclei on the goethite surface controls the actual dehydroxylation kinetics. The thermal dehydroxylation of kaolinite is another example – it were described either by the diffusion kinetic law or by JMAYK equation, in both these cases with the deviations in the final stage of the reaction [5, 6]. These examples demonstrate that the procedures for processing heterogeneous kinetic data must be carefully chosen and applied.

Beside physically bound water, pure and especially aluminuous goethites contain also non-stoichiometric water in their crystal lattices [4, 7, 8, 9]. Their dehydroxylations primarily yield hydrohematite, a hematite-like phase with excess water in the crystal lattice [7] :

$$\alpha-FeOOH \xrightarrow{>180^{\circ}C-H_2O} \alpha-Fe_{2-\delta/3}(OH)_{\delta}O_{3-\delta}$$
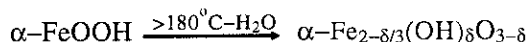
with $0<\delta<1$. As a result, it is not entirely trivial to establish an equilibrium mass loss that must be known for the calculation of reaction conversion. Moreover, the further dehydroxylation of hydrohematite occurs very slowly below 600 °C, that causes a very slow mass loss after goethite decomposition (see 'mosaic' plots of $\log(-\log(1-y))$ *vs.* $\log(t)$ [1]). The reaction progresses from the external surface or from the crystal edges [3, 4] toward particle cores as in the case of the GRO kinetics. The most likely, the larger the amount of crystal defects, edges, and hematite nuclei on the original goethite surface, the more the reaction course resembles the GRO law of a simple surface reaction [3]. However, the initial kinetics of the dehydroxylation may be expected to deviate from the main part of the reaction conversion as observed by Koga *et al.* [3].

Thermal dehydroxylation of pure and Al-substituted goethites has already been described [1] using the JMAYK equation and between one and three linear portions on the kinetic fit were obtained indicating a change from diffusion to random-nucleation control. The originally used 'time-to' method [1, 6] based on the assumption of a unique dehydroxylation-kinetic law in the whole range of reaction conversion, yields activation energy being a function of temperature and conversion. Now we present different data processing using the GRO kinetic law. We show why the 'time-to' method has not yielded a single value of E_A.

Experimental

The properties of synthetic goethites with and without Al substitution used for this study were fully described by Ruan and Gilkes [9]. The isothermal dehydroxylation was performed as already described [1] : the sample was preheated at 110°C to remove adsorbed water until the mass was constant, then heated at rate 80°C min^{-1} to desired temperature in flowing air and maintained for 4 h. In the present work, the data are processed by the kinetic approach described [10, 11].

Results and discussion

Figure 1 is the plot derived from thermal transformation of pure goethite (0 mol% Al) to hematite obtained from XRD line broadening, which represents the thermal transformation trend of the samples used in the present study. The value $y=0.3$ was chosen for goethite and $y=0.8$ for hematite. The d-spacing of goethite did not change apparently until heated over 220°C and 260°C for the $y=0.3$ (Fig. la). The d-spacing of hematite at a y value of 0.8 decreases systematically as shown in Fig. lb. Consequently the decrease in d-spacing results in the reduction of unit cell dimension parameters. The decomposition of goethite structure is indicated by the decrease in intensity of diffraction lines (Fig. lc) and the increase in width at half height (WHH) (Fig. ld). Meanwhile, an increase intensity in Fig. lc and a decrease in WHH in Fig. ld indicate the progress of formation of hematite and its crystallographic growth.

The transmission electron micrographs (TEM) of goethites and their dehydroxylation products are shown in Fig. 2. They are composed of nanocrocrys-
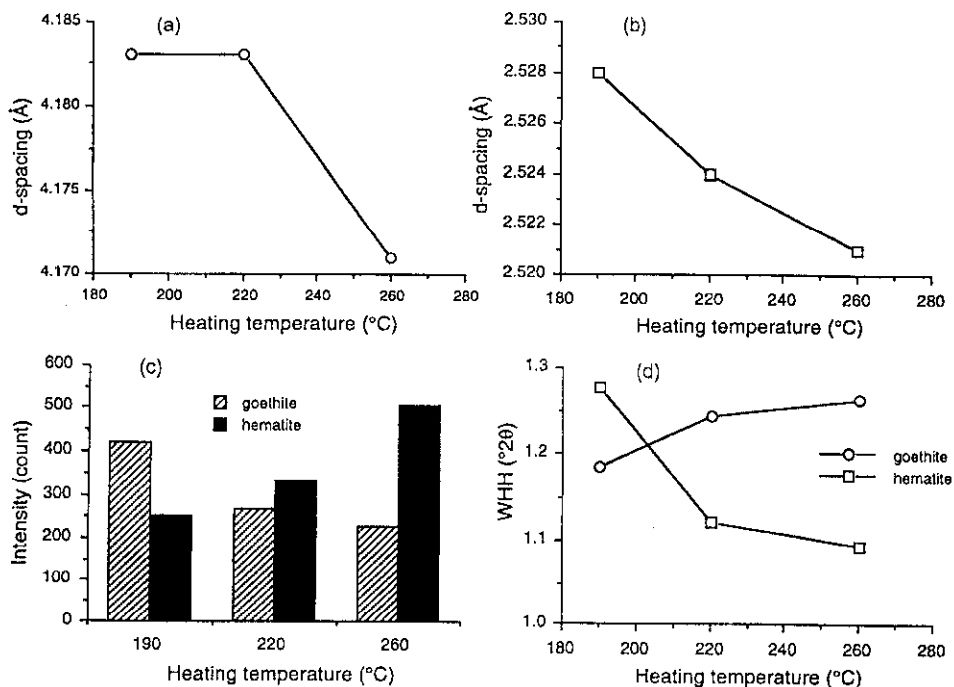
Fig. 1 The change in d-spacing, intensity and width at half high (WHH) of 0 mol% Al-substituted goethite and hematite derived from XRD line broadening as affected by heating temperature, (a) d-spacing of goethite, (b) d-spacing of hematite, (c) intensity of goethite and hematite, (d) WHH of goethite and hematite, the y value of 0.3 was chosen for goethite and 0.8 for hematite
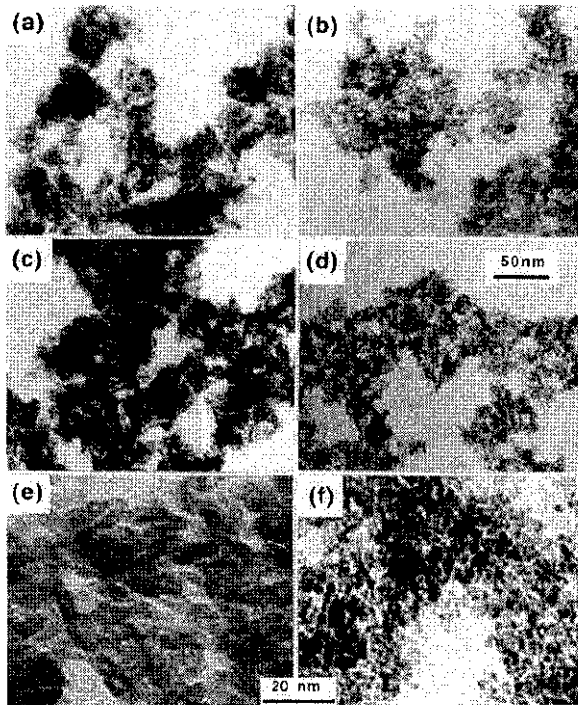
Fig. 2 Transmission electron micrographs of goethites and their dehydroxylated products;
(a) 0 mol% Al heated at 110°C, (b) 20 mol% Al heated at 110°C, (c) 0 mol% Al heated
at 220°C, (d) 20 mol% Al heated at 240°C, (e) 0 mol% Al heated at 240°C and (f)
30 mol% Al heated at 250°C. Bar in (d) represents scale for all samples except (e) and (f)

talline particles with a size between 7 and 10 nm. The non-substituted goethite
and hematite are composed of lath-like crystals, whereas the Al-substituted ones
have more equant shapes. The shape of dehydroxylated products does not alter
within such low heating temperatures 180–260°C although the changes in crystal
size, unit cell dimensions, and speciftc surface areas were obviously observed [7,
9]. The variation of the mean coherence length (MCL) measured as crystal size
from XRD line broadening and shown in Fig. 3 is identical to the values of crys-
tal size obtained from TEM (Fig. 2). The decrease of goethite MCL and increase
of hematite MCL during the structural transformation are illustrated in Fig. 3.

At each given temperature and in the entire conversion range, the dehydroxy-
lation rate continuously decreases that enables to neglect the nucleation kinetics.
The samples lose the first 1–2% of their mass very quickly due to the loss of
physically bound water. This reaction stage is difficult to describe and hence it is
not involved in further data processing.

Monotonously decreasing reaction rate enables to apply the GRO kinetic law.
We have chosen the form that is used in dissolution analysis [10, 11]

$$\frac{dy}{dt} = k(1 - y)^{\gamma}$$

Here, the conversion is calculated by the relationship

$$y = \frac{W}{W_{eq}}$$

where W and W_{eq} are actual and equilibrium mass losses. W_{eq} depends on the stoichiometry of both original goethite and resulting hydrohematite. At each temperature k, γ, and W_{eq} are estimated by the least squares method in the conversion range 20–95 %. Results are given in Table 1.
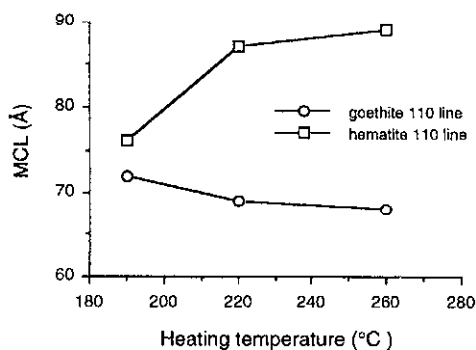

Fig. 3 Mean coherence length (MCL) derived from XRD 110 line for goethite and hematite respectively, representing crystal size as affected by heating temperature from TG measurement

The obtained rate coefficients were processed using the Arrhenius equation (Fig. 4). The resulting values of the activation energies given in Table 1 are in a good agreement with about 140 kJ mol^{-1} obtained recently by Koga *et al.* [3] for pure, highly crystalline goethite, including samples after hydrothermal ageing, and with $\approx$125 kJ mol^{-1} according to Ref. [13] also for pure goethite. This agreement is remarkable particularly with respect to a much lower crystallinity of the goethites studied here. Schwertmann and Cornell [4] reviewed a surprisingly high scatter in the reported activation energies of goethite dehydroxylation, 88 to 247 kJ mol^{-1}. It is hard to explain such a considerable scatter only by a different crystallinity of the goethite samples. Rather a possible inconsistency and ambiguity of kinetic models employed by various authors could be suspected.

Our results show that the equilibrium mass losses W_{eq} significantly exceed the stoichiometric amount of H$_2$O/OH^{-}, that is in line with the findings of Wolska and Schwertmann [8]. The total excess OH^{-} during the thermal transformation of goethite to hematite can be estimated also from thermogravimetry by subtracting the amount of water released based on theoretical calculation from the mass loss at 260°C for around 200 h [1]. Figure 5a shows that this maximum mass loss is

Table 1 Results of fitting the isothermal dehydroxylation curves by the GRO kinetic law

$T/^{\circ}C$	0 mol% Al			10 mol% Al		
	W_{eq}	$10^3 k/s^{-1}$	γ	W_{eq}	$10^3 k/s^{-1}$	γ
190	12.2	0.41	1.15			
200	11.9	1.27	1.20	13.6	0.66	1.44
210	11.4	1.91	0.82	13.6	1.31	1.25
220	11.7	4.65	0.94	13.6	2.48	0.99
230	11.6	6.54	0.74	13.6	4.99	1.17
240	12.0	12.6	0.73	13.7	8.83	0.99
250	$E_A = 130(8)$ kJ mol^{-1}			13.5	11.3	0.69
				$E_A = 132(2)$ kJ mol^{-1}		

$T/^{\circ}C$	20 mol% Al			30 mol% Al		
	W_{eq}	$10^3 k/s^{-1}$	γ	W_{eq}	$10^3 k/s^{-1}$	γ
210	15.7	1.58	2.5			
220	15.7	1.80	1.9	18.5	1.56	2.6
230	15.4	3.77	1.6	17.5	2.66	2.2
240	15.4	6.60	1.7	16.9	5.48	1.8
250	15.3	12.3	1.6	16.9	7.67	1.6
260	15.1	18.9	1.4	16.9	13.5	1.6
	$E_A = 128(5)$ kJ mol^{-1}			$E_A = 123(7)$ kJ mol^{-1}		

15.1, 15.9 and 17.6% for Al substitution of 10, 20 and 30 mol%, which is by 4.7, 5.1 and 6.2 higher compared with 10.4, 10.8 and 11.4% for stoichiometric $Al_xFe_{1-x}OOH$. From Table 1 follows that the mass losses W_{eq} obtained by fitting dehydroxylation kinetic curves are in a reasonable agreement with such gravimetric estimations.
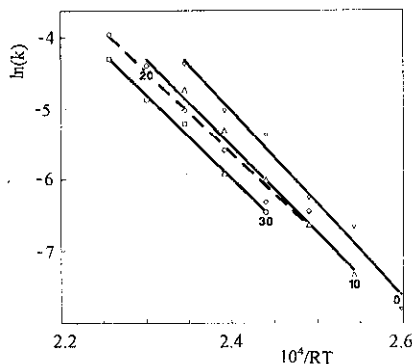
Fig. 4 The Arrhenius plot of the rate coefficients obtained by the GRO kinetic law. The numbers denote mol% of Al substitution in the goethite lattice

The observed mass loss is linearly related with E_A obtained using the GRO kinetic law (Fig. 5a). A similar linear relationship is obtained by plotting E_A against mole% of Al (Fig. 5b). The pure goethite was excluded from the graph in terms of the crystal shape effect. Because excess OH^- in the structure of goethite and hematite are linearly related with the amount of Al substitution ($r^2=0.98$, $P=0.95$) (Fig. 5c), the decrease in E_A with increasing Al content could be attributed to a larger amount of excess OH^-. Their incorporation into the structure may weaken the (Fe, Al)–OH bonds and thus less activation energy is needed for the
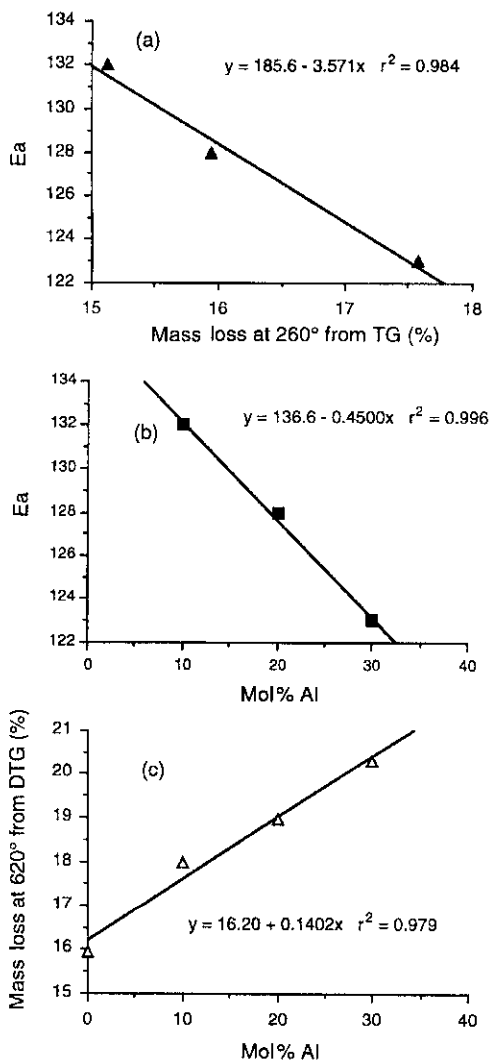

Fig. 5 Activation energy E_a as a function of (a) mass loss and (b) Al substitution, (c) mass loss at 620°C measured by DTG is linearly related with Al substitution

dehydroxylation. However, using the 'time-to' method, this decreasing trend in E_A values with the increasing Al content agrees only for operating temperatures below 220°C and conversions below 0.3 [1]. The difference in E_A between the kinetic model used in the previous [1] and the present study may hence deserve further work.

As a result of the mentioned non-stoichiometry, the overall thermal decomposition of goethite could be considered a chain of three subsequent and/or simultaneous steps

1 – dehydratation of physically sorbed water at around 100°C the most likely according to GRO kinetics (as for hydrated γ–FeOOH [14]); the step is probably accompanied by the loss of a part of excess structure water α–FeOOH,

2 – the above described hematite-like phase formation that is controlled by a chemical reaction,

3 – and a diffusion-controlled step of primary hematite dehydratation.

From a theoretical point of view, such mixed kinetics requires to pay a particular attention to the data processing and interpretation, because either deviations from common kinetic models or even non-constant E_A could be expected [15]. With respect to this complexity, the present approach is based on a relatively universal and very flexible kinetic function – GRO with a free value of the apparent reaction order γ, and we hence resigned to interpreting its value in the sense common in thermal analysis. The GRO function enables just safely extrapolate the reaction rate to the initial reaction stage, where, at least, the surface is well defined, and where the impact of mixed kinetics should be less pronounced.

The changes in observed values of γ with temperature (Table 1) exclude the correct utilisation of the 'time-to' method [1], master plots, and other procedures based on assumption of a unique function $f(y)$ independent on the reaction temperature [12]. This conclusion may seem surprising with respect to the popularity of fitting procedures widely employed in thermal analysis. However, a certain dependence of γ on an enforced reaction rate was observed in reductive electrochemical dissolution of iron oxides, too [10, 11]. The lack of experimental data has not yet allowed to explain this dependence, but it may illustrate a more general phenomenon, the most likely mixed kinetics. Here, γ decreases with increasing temperature toward the values 0.5 to 1 expected for a surface chemical reaction of polydisperse acicular crystals [11]. In other words, the higher dehydroxylation temperature, the closer is the reaction course to the kinetic law of a surface chemical reaction. At lower temperatures, an unknown additive contribution to the reactivity distribution function may be supposed [11]. This is especially valid for the goethites with 20 and 30 mol% Al. In any case, it seems to be more reasonable to suppose departures from simplified kinetic functions $f(y)$ (see above) than to explain E_A varying with an actual conversion.

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