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DIFFERENTIAL THERMAL ANALYSIS OF UNSUPPORTED AND SUPPORTED IRON OXIDE CATALYSTS *

IN recent years, the technique of Differential Thermal Analysis (DTA) has been employed as a tool in the structural studies of catalysts of technical importance.[1] To characterize some of the nickel hydrosilicates formed during the preparation of nickel-silica catalysts, Voorthuijsen and Franzen[2] used this technique as an adjunct to the well-established X-ray diffraction method.[3] In the present investigation, the same technique has been extended to understand the thermal behaviour of some unreduced iron catalysts.

The apparatus employed for the determination of thermal analysis curves was essentially the same as described by Bhattacharya and co-workers.[1] The following samples have been studied :

1. Fe_2O_3 I, prepared by the decomposition of pure hydrated ferric nitrate at 400° C.
2. Fe_2O_3 II, prepared by the precipitation of ferric nitrate as hydroxide in solution by ammonia followed by drying of the precipitate at 110° C. for several hours.
3. Fe_2O_3-Kg II, prepared by the precipitation of ferric nitrate as hydroxide by ammonia in a slurry of Kieselguhr (with surface area of 44 m.² per gram) followed by drying of the precipitate at 110° C. for several hours.
4. Fe_2O_3-Kg VI, prepared by the same method as Fe_2O_3-Kg II, but in presence of Kieselguhr (with surface area of 1·5 m.² per gram).
5. Fe_2O_3-Kg IV, prepared by mixing a slurry of Kieselguhr (with surface area of 44 m.² per gram) with a slurry of ferric hydroxide obtained by precipitation from ferric nitrate, followed by drying of the precipitate, at 110° C. for several hours.

The differential thermal analysis curves for the above samples obtained using chromel-alumel thermocouples with a rate of heating of 25° C. per minute, are shown in Figs. 1 and 2.
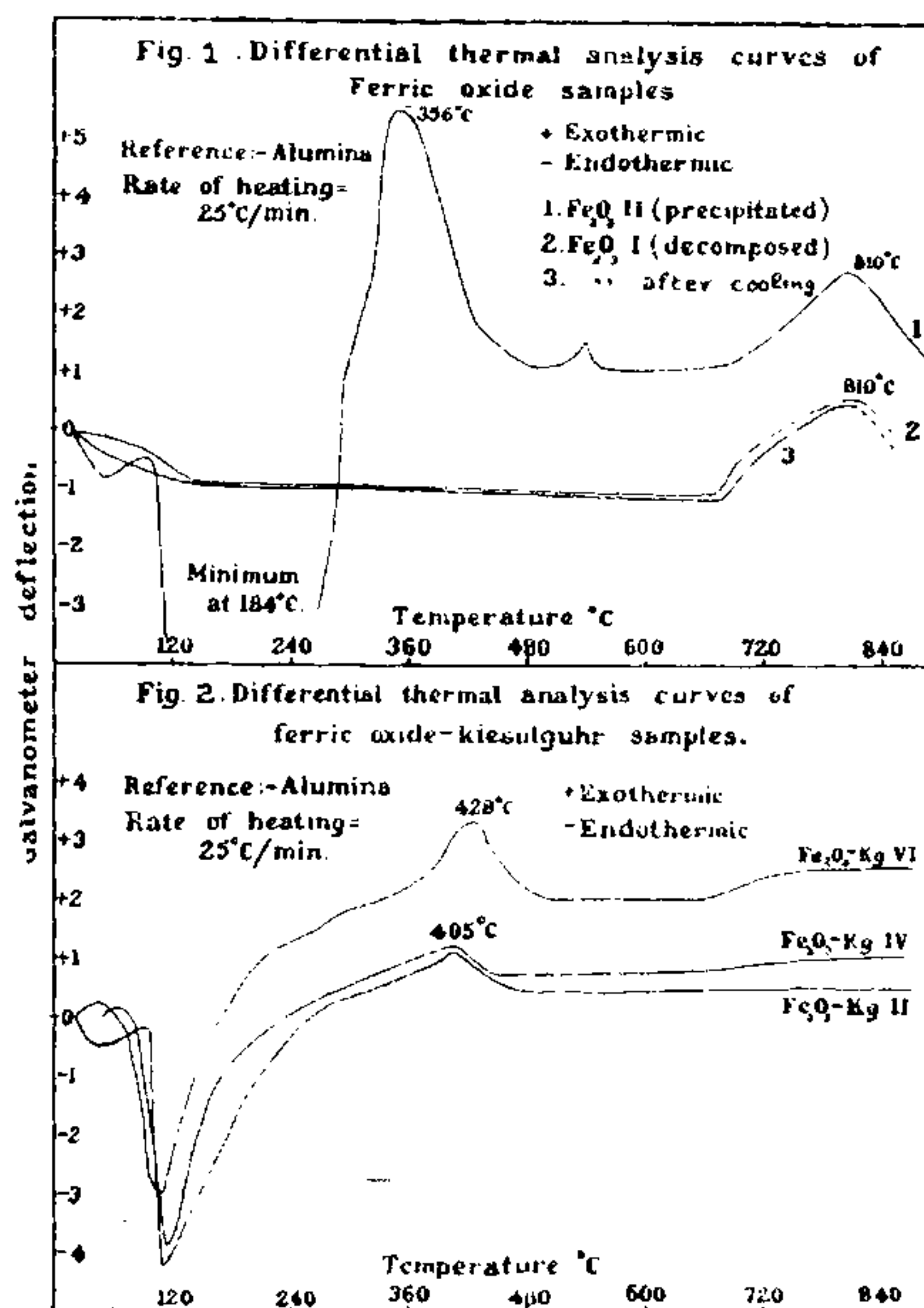
FIGS. 1-2

The DTA curve of Fe_2O_3 I showed an exothermic reaction beginning at 680° C. reaching a maximum at 810° C. To test the reversibility of this reaction, the sample was cooled to room temperature and the experiment repeated. The exothermic reaction was again reproduced. The thermocouples were found unattacked even after repeated runs.

Fe_2O_3 II on heating undergoes several structural changes as revealed by several peaks in the DTA curve. The endothermic peak at 184° C. is ascribed to the expulsion of adsorbed water from the ferric oxide gel accompanied by the formation of amorphous Fe_2O_3. The crystallisation of this amorphous Fe_2O_3 to α-Fe_2O_3 takes place around 250° to 450° C. as indicated by the exothermic peak at 356° C. Bhattacharya and co-workers[1] who prepared ferric oxide gel by a similar method noticed a low temperature endothermic reaction between 140-200° C. due to the expulsion of adsorbed

water followed by an exothermic reaction between 360° and 465° C. due to crystallization of α-Fe₂O₃ and these results were confirmed by X-ray diffraction studies. Lodling and Hammell[4] who have also studied the thermal behaviour of aged ferric oxide gels employing DTA and X-ray techniques, have reported the formation of goethite (α-FeO.OH) and also small amount of lepidocrocite (γ-FeO.OH) in the initial stages.

During the preparation of Fe_2O_3 II employed in the present investigation, the ferric hydroxide was not allowed to age, so that the formation of α-FeO.OH could not be expected. It is, however, possible to expect the formation of traces of γ-Fe_2O_3 along with α-Fe_2O_3. The small exothermic peak noticed around 540° C. may be due to the conversion of γ-Fe_2O_3 to α-Fe_2O_3 as reported by Lodling and Hammell. There is no reference in literature for the occurrence of an exothermic reaction for Fe_2O_3 samples prepared by diverse methods around 800° C. Further work is in progress to characterise the reversible exothermic reaction at 810° C.

The DTA curves of the supported ferric oxide samples show a single endothermic peak around 110° C. due to expulsion of adsorbed water and an exothermic peak around 400–430° C. due to the crystallization of amorphous Fe_2O_3. Comparison of the DTA curves of unsupported and supported ferric oxide samples shows that the introduction of Kieselguhr as support results in the suppression of peaks obtained at 540° C. and 810° C., which can possibly be ascribed to the relatively small amount of Fe_2O_3 (about 20–30% of the total weight) in the samples. The introduction of support facilitates the easy removal of adsorbed water as seen by the shifting of the endothermic peak from 184° C. to around 110° C., but does not help the crystallization of amorphous Fe_2O_3 (because of the dispersion of the oxide on the surface of the support) which is indicated by the shift of the exothermic peak from 356° C. to a higher temperature (400–430° C.). The absence of a second endothermic peak in the DTA curves of Fe_2O_3-Kg samples is indicative of the absence of iron hydrosilicates in them.

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KINETICS OF OXIDATION OF ALLYL ALCOHOL BY CERIC NITRATE IN NITRIC ACID

THE oxidation of alcohols by ceric salts has attracted the attention of many workers in recent years.[1-4] The work has been concentrated chiefly on the oxidation of various alcohols by ceric perchlorate in perchloric acid or ceric sulphate in sulphuric acid. Not much work has been done using ceric nitrate in nitric acid. The two outstanding papers in this field are the one by Duke and Forist[5] on the oxidation of 2, 3-butanediol by ceric nitrate, and the other by Shorter[6] on the oxidation of acetone. In our earlier paper[7] the results on the oxidation of isopropanol and sec. butanol, by ceric nitrate in nitric acid, were presented and discussed. In this paper, the results on the oxidation of allyl alcohol by ceric nitrate in nitric acid are presented. In general, reactions in this medium resemble those in perchloric acid. The oxidation of allyl alcohol by ceric nitrate was found to be faster as compared to n-propanol.

The reaction has been followed by determining the rate of ceric disappearance by titrimetry with excess of ferrous ions and back titration with standard ceric ammonium sulphate using methyl red as the indicator. The rate is first order with respect to cerium (iv) in the initial stages of the reaction. The pseudo unimolecular rate constants obtained under the conditions of allyl alcohol $\gg$ Ce(iv) gives an order of 0·72 for allyl alcohol. The plot of 1/Rate Vs. 1/[Allyl alcohol] was found to be linear. The rate was found to increase with decrease in H⁺-ion concentration at constant ionic strength, and inversely as the square of the nitrate-ion concentration. The results in the present investigation are similar to the results of our earlier work[7] on the isopropanol oxidation. There is both kinetic and spectrophotometric (cf. Ardon[2]) evidence to show that a 1 : 1 complex is formed between ceric nitrate and allyl alcohol before fission of the O-H bond and electron transfer. The mechanism seems to be as follows :