

A Comparison of the Thermal oxidation of Nickel and Cobalt Impregnated Charcoal

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Summary: Pure charcoal was impregnated with nickel and cobalt. The effect of metal impregnation on the thermal oxidation of charcoal was studied and compared by employing thermogravimetry and differential thermal analysis. The results show the impregnation of cobalt results in a significant decrease in the decomposition temperature of charcoal. The energies of activation for decomposition, calculated from the thermogravimetric curves, are 42.96, 38.61 and 30.58 kJ/mol for pure, nickel and cobalt impregnated charcoal respectively.

Introduction

Activated charcoal is used as an adsorbent [1,2] catalyst [3,4] and catalyst support [5]. The marked characteristics of activated charcoal include micro porous structures, high purity and selective adsorption [6]. Impregnation of metals results in the modification of chemical properties of activated charcoal [7]. This effects the reactivity and selectivity of the surface in the catalytic reaction. This paper aims at elaborating the thermal properties of nickel and cobalt impregnated charcoal. The effect of these metal impregnation on the stability of charcoal towards oxidation have been studied and compared by employing thermogravimetry (TG) and differential thermal analysis (DTA).

Results and Discussion

The TG curves of pure, nickel and cobalt impregnated charcoal are depicted in Figure 1-3 respectively. The loss of moisture adsorbed during the processing of these samples appears as initial weight loss. The sample of pure charcoal remains stable upto 415°C after which it starts to decompose. The samples of charcoal impregnated with nickel and cobalt start to decompose at 290°C and 270°C respectively. It shows that the impregnation of metal in charcoal results in the lowering of its thermal stability.

The DTA curves for these samples are reproduced in Figures 1-3. The DTA curve of pure charcoal has a broad endotherm at 132.4°C due to dehydration. It is followed by an exothermic peak at 510°C proceeded by small entothermic heat effect at 661.5°C and

810°C. These appear as a result of decomposition of the sample. The charcoal samples impregnated with nickel and cobalt have endotherm at 132.3°C and 129.1°C respectively. The exothermic decomposition in air [8] is evident at 410°C and 362°C for nickel and cobalt impregnated charcoal respectively. It is evident that the impregnation of metal on charcoal results in the lowering of start of degradation temperatures.

The results obtained by TG and DTA were verified by calculating the activation energies for decomposition (AED) from the TG curves. AED were calculated by employing the Horowitz's method [9]. In this method in $\ln \ln (W-W_f/W_o-W_f)$ versus θ is plotted as shown in Figure 4. When W_o , W and W_f are the initial weight, weight at any time t and final weight respectively. $\theta = T - T_s$, where T is the temperature at weight W and T_s is the temperature when $(W-W_f/W_o-W_f)$ equals $1/e$ (0.368). The gradient thus obtained is:

$$\text{slope} = E/RT_s^2$$

where E is the activation energy R is the gas constant. The computed [10] values of AED for these samples are presented in Table-1.

Table-1: Activation energies values of metal impregnated charcoal.

Sample	Activation energy (kJ/mol)	
	Dehydration	Decomposition
Pure charcoal	62.0	43.0
Ni-charcoal	64.4	38.6
Co-charcoal	68.0	30.6

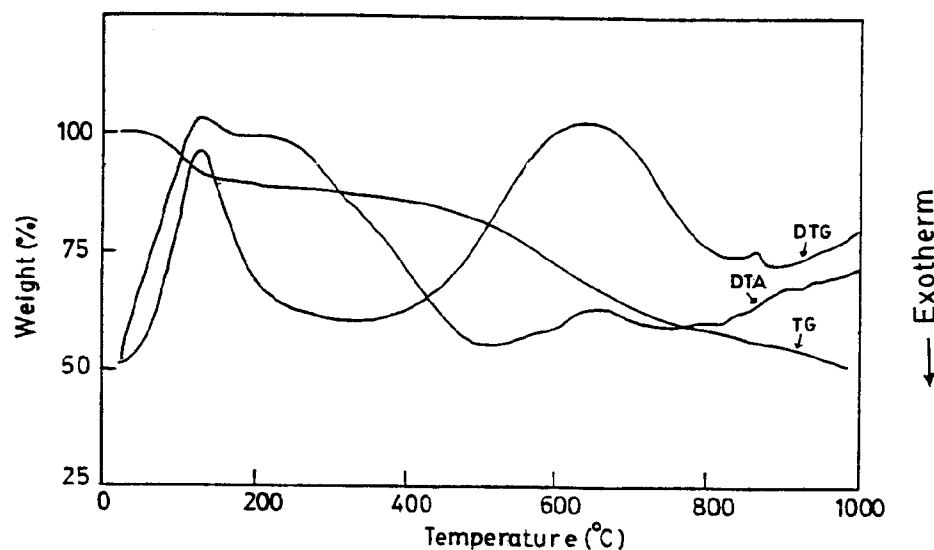


Fig. 1: TG and DTA curves of charcoal.

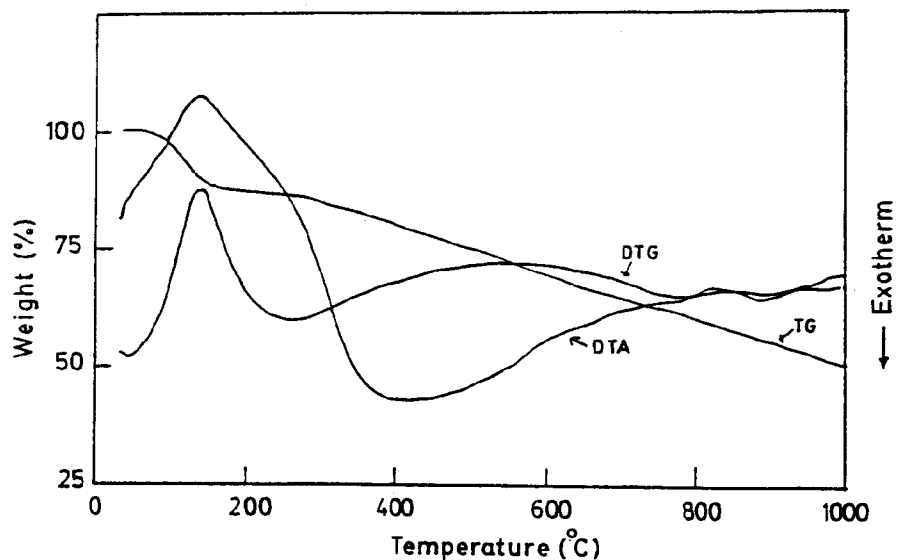


Fig. 2: TG and DTA curves of nickel impregnated charcoal.

Dehydration step in all the three samples required energies falling in the range of 62-68 kJ/mol. The pure charcoal sample has AED of 43 kJ/mol. However the impregnation of metal results in lowering of AED. Cobalt impregnated charcoal has the least value i.e., 30.6 kJ/mol when compared to pure charcoal and nickel impregnated sample. These computed values of energies for

decomposition supplement the preceding discussion regarding the lowering of thermal stability of charcoal upon impregnation. Similar trends have been reported by McKee [11] during the studies on catalytic thermal decomposition of pure graphite. The catalytic effects of these metal salts on charcoal can be explained on the assumption that mobile oxygen atoms formed on the metal surface rapidly

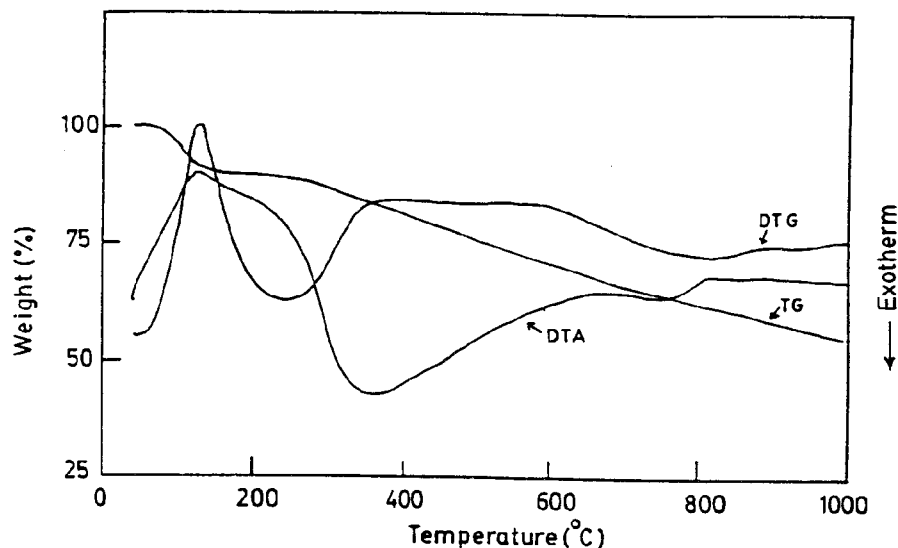


Fig. 3: TG and DTA curves of cobalt impregnated charcoal.

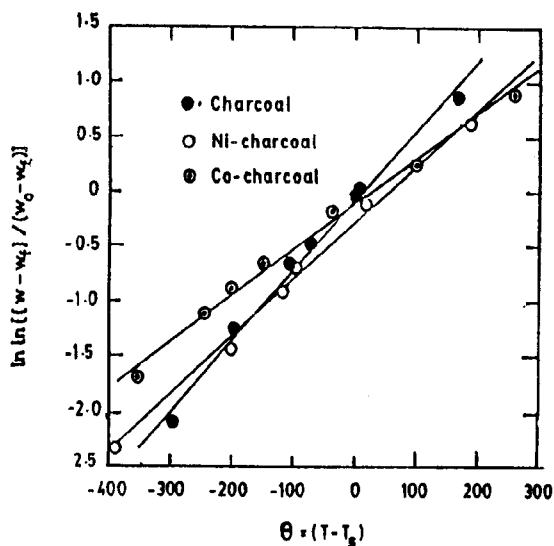


Fig. 4: Plot for the calculation of activation energies for decomposition.

migrate to the metal-carbon interface causing gasification of carbon substrate in the vicinity of catalyst particles. The details of this generalized oxygen transfer mechanism have been elaborately described by Walker *et al.*, [12] and Lewis [13].

It can be concluded from the above discussion that the stability of charcoal is lowered upon impregnation of nickel and cobalt due to the catalytic activity of these atoms. The order of stabilities is:

charcoal > Ni-charcoal > Co-charcoal.

Experimental

Chemical used

Activated charcoal: BDH, item No. 33032; cobalt (II) nitrate hexahydrate: Fluka, item No. 60833; nickel(II) nitrate trihydrate: Fluka, item No. 61197.

Preparation and characterization of metal impregnated charcoal samples

5.0g of activated charcoal were soaked in 100 ml of 2.0 % W/V metal ions solutions for 8.0 hrs. The reaction mixtures was heated at 100°C to a slurry. The mixtures were then dried in a vacuum oven for 1.0 hr. The blank charcoal sample was similarly treated with deionized water. The details of surface area and porosity measurements are described in a previous publication [14]. A wavelength dispersive x-ray fluorescence model SRS 200 manufactured by Siemens, Germany was used for the verification of metal content in the charcoal samples. The metal content for these samples were found to be $1.98 \pm 0.3\%$.

Thermal analysis

TG and DTA curves were recorded from ambient temperature to 1000°C on a NETZSCH simultaneous thermal analyzer model STA-429. 40

mg of each sample were heated in air at a heating rate of 20°C/min.

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