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NICKEL CATALYZED LOW TEMPERATURE GASIFICATION OF GRAPHITE BY CARBON DIOXIDE

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Gasification of various graphites mechanically mixed with nickel catalysts by carbon dioxide was carried out in a thermobalance at temperatures up to 1000 °C. It was observed that some graphites gave large weight loss in the low temperature region of 500-750 °C. The weight loss in this region were increased with increase of the catalyst loading until graphite was completely gasified.

Gasification of carbonaceous materials with nickel catalysts in the low temperature range of 500-750 °C has attracted much interest in recent gasification studies because it allows a fair drop in the operating temperature and yet greater gasification rate can often be obtained compared with those above 800 °C.1) Such low temperature gasifications have been successfully conducted for reactive carbon species such as activated carbon,2,3) deposited carbon,4,5) and brown coal,6,7) by use of nickel catalysts. On the other hand, it is said that this reaction is very difficult to occur for inactive carbons graphitized or heat-treated at high temperatures. But the authors lately found that phenol-formaldehyde resin char (PFC) heat-treated at 1000 °C in N_2 could be gasified by CO_2 to a considerable extent with the aid of nickel catalyst even in the low temperature region of 500-800 °C.8) In this connection, the present paper describes the successful low temperature gasification of graphite by CO_2.

Four artificial graphites (abbreviated as TK, LZ, SP-2, and TSP-2) and five natural ones (KD-1, KD-2, WK, R-1, and SP-1) were used as carbon materials in this study. Their properties are given in Table 1. All the graphites were ground to pass through 200 Tyler mesh followed by mixing with nickel compounds in a mortar grinder for 1 h. Nickel catalysts employed here were the following five:

Table 1. Properties of graphite samples

Graphite	Code	Fixed Carbon (wt%,dry basis)	Ash (wt%,dry basis)	Crystallite Size[b] Lc(Å)	Specific Surface Area(m^2/g)
Kishida(soil)	KD-1	81.8	18.0	260	21
Kishida(scale)	KD-2	86.2	11.7	930	11
Wako	WK	85.5	9.8	1300	13
Nippon Carbon	R-1	98.5	1.2	820	12
Nippon Carbon	SP-1[a]	99.5	0.02	1000	11
Tokai Carbon	TK	99.7	0.3	540	14
Lonza	LZ	99.5	0.06	650	9
Nippon Carbon	SP-2[a]	99.5	0.01	470	13
Tokai Carbon	TSP-2[a]	99.8	0.01	370	12

a) Spectroscopic grade. b) From width of X-ray diffraction lines.

$Ni(CH_3COO)_2\cdot 4H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $NiC_2O_4\cdot 2H_2O$, $Ni_3CO_3\cdot(OH)_4\cdot 4H_2O$, and NiO. The content of nickel added was 0.5 atomic % (2.6 wt%) against carbon atoms in each graphite unless otherwise stated. The catalytic activity of nickel or reactivity of graphite was evaluated by using a thermobalance. The thermogravimetric (TG) measurement was carried out for the graphite-nickel mixture of 10 mg using a constant heating rate of 10 °C/min up to 1000 °C. The flow rate of CO_2 was 250 ml/min at an atmospheric pressure.

TG curves obtained for various graphites added with nickel acetate are shown in Fig. 1. The weight loss dose not include that of the catalyst, since its thermal decomposition finishes below 400 °C. As all the graphites gave no weight loss up to 900 °C in the abcence of the catalyst, the addition of nickel was obviously effective in accelerating the gasification by CO_2. For six graphite samples of R-1, TK, LZ, SP-2, TSP-2, and SP-1, their gasification profiles appeared to be separated into two regions: a major weight decrease in the range of 500-750 °C, and a minor weight decrease above 800 °C. A similar TG

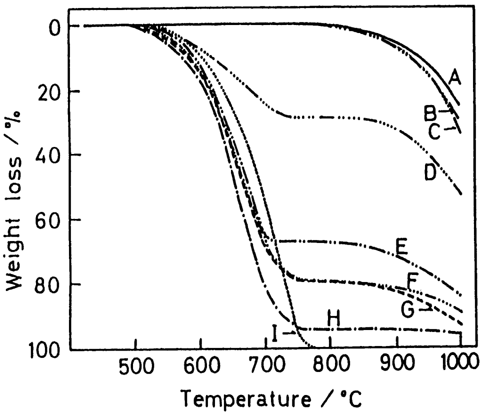

Fig. 1. TG curves for various graphites added with nickel acetate in CO_2. A,KD-2; B,WK; C,KD-1; D,R-1; E,TK; F,sp-2; G,LZ; H,TSP-2; I,SP-1.

pattern was observed for PFC previously used.8) The weight loss in the lower temperature region reached approximately 30%(R-1), 70%(TK), 80%(LZ), 80%(SP-2), 95%(TSP-2), and 100%(SP-1), respectively. It is quite surprising that carbons graphitized at extremely high temperatures around 3000 °C could easily be gasified even below 750 °C by the simple mechanical mixing with nickel catalyst, although impregnation of graphite with $Fe(NO_3)_3$ solution was also reported to enhance the gasification rate in almost the same temperature range.9) In contrast, KD-1, KD-2, and WK (A, B, and C in Fig. 1) gained small weight loss only above 800 °C. This behavior different from that for the preceding six graphites may be attributed to their higher ash content as seen in Table 1. A possible deactivation of nickel catalyst by inorganic impurities in graphite will be supported by the fact that the extent of gasification of graphites used in the low temperature region increased with decreasing the ash content. But ash content cannot be the only factor affecting the activity of the catalyst. Further examinations are necessary to explain this ploblem fully.

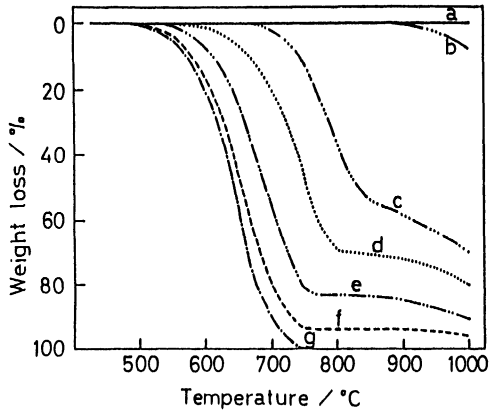

Fig. 2. Effect of the loading of nickel acetate on the gasification for TSP-2. a,0%; b,0.025%; c,0.05%; d,0.1%; e,0.25%; f,0.5%; g,1.0%. (%:atomic)

According to the nickel-catalyzed gasifications by steam7) and H_2,10) the reaction progress in the low temperature region was strongly dependent on the catalyst loading. Similarly effective increase of the nickel loading was observed as is demonstrated in Fig. 2. That is, no low temperature gasification occurred at the loading of less than 0.025 atomic % (0.13 wt%), and more than 0.05 atomic % (0.26 wt%) loading contributed to increasing the amount of weight loss accompanying the drop of beginning temperature of weight loss. At 1.0 atomic % (5.2 wt%) loading the weight loss reached 100% below 750 °C. The complete gasification also occurred for LZ and TK at higher nickel loadings of 2.0 atomic % (10.4 wt%) and of 4.0 atomic % (20.8 wt%), respectively. It has been recognized that nickel catalysts lose their activities during the gasification by steam or H_2.2-7,10,11) This phenomenon is considered to be caused by the partial graphitization of unreacted carbon.12) The present results, however, indicate the unlikeliness of such an activity loss of nickel catalyst.

Figure 3 shows that nickel compounds exhibit different catalytic activities with their different type of anions. Additions of oxalate and nitrate brought about considerable weight loss in the low temperature below 750 °C similarly to acetate. But, carbonate and oxide had limited effects of only rapid weight loss at 830 °C and 880 °C, respectively. The order in the catalytic activity of these nickel compounds is closely related to their reducibility to nickel metal in CO_2 as confirmed by temperature-programmed X-ray diffraction.[8] This is commonly accepted that nickel compounds act as a catalyst only in the reduced state.

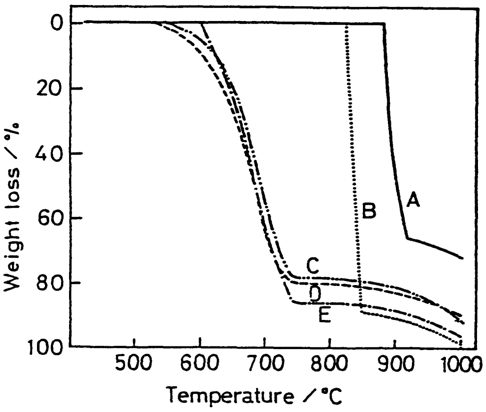

Fig. 3. Effect of various nickel compounds on the gasification for LZ. A,NiO; B,$Ni_3CO_3 \cdot (OH)_4 \cdot 4H_2O$; C,$NiC_2O_4 \cdot 2H_2O$; D,$Ni(CH_3COO)_2 \cdot 4H_2O$; E,$Ni(NO_3)_2 \cdot 6H_2O$.

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