INCREASING GAS SORPTION ONTO CARBON BY MILLING WITH ALUMINA

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Abstract

Graphite milled alone for 50 h shows an increase in gas sorption of a factor of three over unmilled powder. When graphite is milled in the presence of a much harder phase, aluminium oxide, the increase in sorption is much greater with a seven fold increase achieved after 5 h milling. Extending the milling time resulted in increased capacity; an estimated capacity of 2.5 g/ g carbon was achieved after 50 h milling.

Introduction

Activated carbons are used in a number of industrial processes as adsorbents for a wide range of compounds, both organic and inorganic. The capacity for adsorption is highly dependent upon the pre-treatment of the carbon itself and a range of activation processes has been proposed. Earlier work [1-3] has clearly demonstrated that very large increases in sorption capacity can be obtained by ball milling graphite and activated carbons for extended periods. The sorption was a function of milling time with a milling time of 1000 h leading to a loading of around 0.5 g of gas per gram of carbon [1]. The surface area of milled graphite is a function of both milling time and milling atmosphere [4], inert atmosphere leading to the greatest surface area whilst oxygen lead to the lowest area. These results are clouded by the discovery that significant amounts of physio-sorbed and chemisorbed gas are present on as milled carbon powders [2,3]. Therefore, the pre-treatment of the sample prior to surface area measurement by BET is critical in achieving the true surface area. Milled graphite has been increasingly investigated as a possible storage medium for hydrogen [5-9].

It has been shown [10-13] that in two phase systems the crystallite size of the softer phase is more readily reduced. Thus, the majority of the energy transferred during ball impact is used to refine the crystallites of the softer phase. This leads to the conclusion that milling graphite with a harder phase would be likely to lead to greater adsorption capacity for a shorter milling time. A previous letter [14] showed this to be the case with graphite milled with aluminium oxide having a gas capacity of 0.56 g/g compared with 0.15 g/g achieved by milling carbon alone for the same time. Previous work [1] indicated 0.5 g/g was achieved by milling graphite alone for 1000 h.

This paper examines the effect of milling time on the sorption of gas by graphite milled with aluminium oxide.

Experimental Method

The raw materials used were synthetic graphite and crystalline aluminium oxide, both were nominally >99% pure. Samples consisted of either pure graphite or a mixture comprising 3.00 g Al_2O_3 + 4.00 g graphite. Seven grams of powder were loaded into a laboratory scale tumbling mill with five 25.4 mm steel balls, giving a ball to powder mass ratio of 43:1. The mill was then evacuated to ~10^{-2} Pa and backfilled with argon during milling. After the allotted milling time, the mill was opened to air and a sample transferred to an aluminium oxide crucible. The crucible was then heated at 20°C/min to 1200°C under a flowing argon atmosphere in a thermogravimetric analyser.

To assess the amount of abraded iron in the carbon samples obtained after milling, the milled powders were leached in 0.1M hydrochloric acid for 2 h. The mass loss during acid leaching was attributed to iron.

Results and Discussion

The mass loss in argon as a function of temperature is shown in Fig. 1.
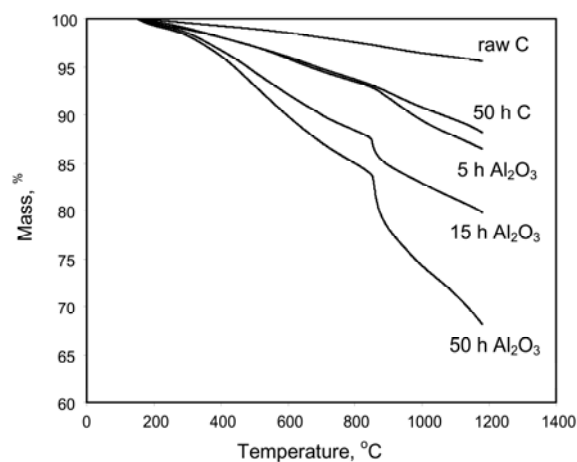

Figure 1. Mass of sample as a function of temperature for graphite samples milled alone for 50 h and for graphite milled with aluminium oxide for 5, 15 and 50 h.

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All samples show an increasing mass loss as a function of temperature. Were this due to adventitious oxygen in the argon (nominally <10 ppm O_2) then all samples would be expected to show the same mass loss profile as the limited oxygen in the system would probably control combustion. A preliminary TGA in air showed that the raw graphite had the same mass loss trend as that presented in Figure 1 until ~500 ºC where an increasing rate of mass loss indicated that combustion started resulting in a final mass of ~0.8% at 1000ºC. Similar runs with the other as-milled samples showed combustion starting at around 300 °C for all samples. Were the mass loss in Figure 1 due to combustion then there would have been a change in rate of mass loss at 500 ºC for the unmilled graphite and at 300 °C for the other samples.

From this data it appears that milling graphite for 50 h has a similar effect to milling for 5 h with aluminium oxide. However, the above data does not take into account the mass of aluminium oxide in the powder; if this were removed then the sample milled with aluminium oxide has a very much greater sorption capacity. It is interesting to observe a second stage of mass loss, starting at 850 °C, is present for the samples milled with aluminium oxide but is barely evident even after milling graphite alone for 50 h. The intensity of this stage increased with increasing milling time. In the 50 h sample milled with aluminium oxide there appears to be the onset of a further stage of mass loss at around 1130 °C.

On the basis of the mass loss due to gas adsorption at 1200 °C and the iron content determined by leaching the composition of the as-milled powder can be estimated. Using the sample milled for 50 h with aluminium oxide as the example. For 100 g of the sample milled with aluminium oxide, leaching removed 25.2 g of iron leaving 74.8 g comprising aluminium oxide, gas and graphite. Heating to 1200 ºC resulted in a mass loss of 31.9 g which can be directly attributed to the gas, thus the aluminium oxide and graphite was 42.9 g of the mass after milling. Since the starting mixture contained 4/7 graphite, the actual mass of graphite after milling was 24.5 g. Thus there was 1.30 g of gas per gram of graphite. Table 1 shows the calculated mass of each of the components based on the above calculation. Previous work [1] indicated a ratio of 0.5 was achieved by milling graphite alone for 1000 h. Clearly, milling for only 15h with aluminium oxide present is substantially more effective.

Table 1. Calculated masses of components of the as-milled powders

Sample	Fe	gas	C	Al$_2$O$_3$	g gas / g C
C	0.0	4.46	95.5	0.0	0.05
50h C	9.8	11.90	78.4	0.0	0.15
5h Al$_2$O$_3$	17.3	13.56	39.5	29.6	0.34
15h Al$_2$O$_3$	13.0	20.22	38.2	28.6	0.53
50h Al$_2$O$_3$	25.2	31.91	24.5	18.4	1.30

It is important to note several assumptions were made during this calculation. Figure 1 show that there is still mass loss occurring at 1200 °C therefore the mass of gas within the powder must be higher than this making the mass ratio of gas to carbon an underestimate. It is assumed that starting ratio of C to Al$_2$O$_3$ is constant; however, as will be discussed below, it is likely that there is some loss of carbon during heating. If this is the case the final mass of carbon is actually less than in Table 1, also leading to underestimation of the mass ratio of gas to carbon.

A further heating run up to 1500 °C was performed on the sample milled for 50 h with aluminium oxide, after reaching 1500 °C the temperature was maintained for a further 10 min. This showed that there was an increasing mass loss above 1130°C and another above 1430°C, the mass loss at 1500°C was 40.3%. During the 10 minutes at 1500°C the mass loss decreased exponentially reaching 44.3%; fitting of the exponential decay suggested a total mass loss of around 45.5%. The same calculation as above was made using the mass loss after 10 min at 1500 °C increased the mass ratio of gas to carbon to 2.54 in the as-milled powder.

The identity of the sorbed gas is not certain, however, previous work on similar systems [2,3] has indicated it was CO_2. The gas is likely to be the same in these experiments as the same procedures were followed. Further support for CO_2 comes from the samples milled with aluminium oxide which showed a sudden mass loss at ~850 ºC. It could not be due to reaction with oxygen as noted earlier, but carbon dioxide does react with carbon via the Boudouard reaction to form carbon monoxide. This reaction is thermodynamically favourable above ~700 ºC but may require some activation to occur at an appreciable rate. Previous work with milled carbons [1] did not show such a sudden onset of reaction under argon, indeed the reaction in graphite and activated carbon milled for 1000 h was only discernible as a change in slope. The samples milled for 100 h showed no evidence of reaction. This may be due to greater activation of the underlying carbon resulting in a greater extent of reaction, or a greater content of CO_2 on the surface reacting at ~850 ºC.

Clearly, if this is the reaction occurring then the mass of carbon above 850 °C is decreasing resulting in an even greater capacity than calculated after heating to 1500 °C.

Conclusions

Milling graphite with aluminium oxide results in substantially greater mass losses than for graphite milled alone. A reaction with an abrupt onset occurred at 850 °C but only after milling with aluminium oxide present, this was thought to be due to the reaction between sorbed CO_2 and C. The sorption capacity of the powder was three times greater after graphite was milled alone for 50 h. When aluminium oxide was present a sevenfold increase in gas capacity was achieved after only 5 h. Increasing the milling time when aluminium oxide was present increased the capacity to 1.30 g/g after 50 h. The methods used underestimate the capacity and a value of over 2.5 g gas / g graphite is possible.

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