

Gasification of Carbon Using Calcium Oxide

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Introduction

Extensive investigations of the catalytic action of potassium under the conditions of steam and hydrogen gasification have been reported (1-4). Calcium oxide, as a catalyst, has also been studied under various conditions of temperature and pressure (5,6); however, the nature of the calcium oxide catalysts as a function of time during gasification has not been investigated in detail. It was shown by Lang and Neavel (6) that calcium, in contrast to potassium, was not very active as a gasifying catalyst unless it was very well dispersed by chemical reaction with the organic matter.

Gasification of carbon depends upon the experimental conditions of preparation of the catalyst, as well as on the percent loading, temperature, and time of the gasification reaction. The temperature for maximum gasification rate varies, however, with the type of carbon as well as the catalyst present and its degree of dispersion. The crystallinity and structure of the carbon and the extent of crystallinity of the catalyst also are major factors that influence the rate of the gasification reaction. Because Sphero carb is an extremely pure, high-surface form of amorphous carbon, it has been chosen in this study as the support for the dispersed calcium oxide particles.

In order to understand the carbon-calcium oxide system in more detail, a study was undertaken to prepare dispersed calcium oxide on Sphero carb supports and to measure the change in crystallinity of the catalyst as well as the amount of carbon gasified at 760°C as functions of time. Hence, any changes in catalytic activity of calcium oxide might be correlated with the observed changes in its crystallinity.

Experimental

The Sphero carb particles supplied by Analab (GC012) were of high purity and possessed large surface areas. Impregnation of these particles was accomplished with an aqueous solution of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ Reagent Grade, MCB) to give a final calcium oxide loading of 5% by weight. The concentration of the aqueous solution of calcium nitrate was such that the desired degree of loading could be achieved by the addition of 1 ml solution to the Sphero carb. The loaded sample was dried under an infrared lamp for 2.5 hours and then transferred to a small silica tube which was stoppered at the narrow end with silica wool (Fig. 1). The sample was purged for one hour with dry nitrogen at a flow rate of 100 cm^3/min and then the temperature was raised from room temperature to 540°C. The decomposition of calcium nitrate tetrahydrate was allowed to proceed for 4 hours. The temperature was then raised to the gasification temperature of 760°C. Once this temperature was reached, the gas flow was switched to a hydrogen/water mixture. The flow rate of the hydrogen was 100 cm^3/min and the rate of water injection was 4.82 cm^3/hr . This combination gave a mole ratio of hydrogen to water of 1:1. The water vapor was introduced by injection of distilled water from a syringe pump (Sage Instrument Model 355). The complete reactor as well as the point of injection, which was kept at or above 200°C, is shown in Fig. 1. After the desired time under gasification conditions, the gas flow was switched back to nitrogen and the sample temperature was maintained at 760°C for an additional 30 minutes to

ensure complete dryness. The reaction tube was removed from the furnace and allowed to cool under flowing nitrogen. The sample was weighed immediately after cooling in order to minimize uptake of water. It was stored under vacuum over P₂O₅ until x-ray diffraction patterns could be taken with a Philips Norelco diffractometer using copper radiation ($\lambda_{\text{CuK}\alpha_1}$ =1.5405Å); data were obtained with a graphite monochromator at a scan rate of 1°2 θ /min.

Results and Discussion

It was found that calcium oxide was the species present after gasification of the Sphero carb, was converted to calcium carbonate. This was verified by x-ray diffraction analysis of the products. Conversion of the carbonate to the oxide took place upon heating of the sample to 760°C. X-ray analysis showed that after only 15 minutes of gasification, only calcium oxide is present in the sample. There is no x-ray evidence for the presence of CaCO₃. The sole presence of calcium oxide in the product after gasification indicated that this was the only well-crystallized compound of calcium formed during the gasification process.

A number of gasification experiments were performed on Sphero carb samples containing 5 weight % calcium oxide. The percent of carbon gasified as a function of time is plotted in Fig. 2. There is an increase in the weight loss with time as gasification proceeds, but this loss persists for only one hour after which no additional weight loss is observed. At the end of 60 minutes, approximately 60% of the carbon is gasified and the calcium oxide appears to become deactivated.

There appears to be a correlation between the degree of gasification of Sphero carb, as indicated by weight loss, and the degree of crystallinity of the calcium oxide. Whereas the crystallite sizes were not determined quantitatively, it can be seen from Fig. 3 that as gasification proceeds there is a marked increase in the crystallinity of the catalyst. After only 15 minutes of gasification, the CaO peaks are broad and their sharpness continues to increase until at the end of 60 minutes x-ray diffraction patterns indicate the formation of a well-crystallized product. As loss of carbon takes place during the gasification process, segregation and crystal growth of the catalyst occur. It is apparent that the calcium oxide prefers to segregate rather than redispense to occupy new active sites.

Potassium nitrate was also dispersed on Sphero carb and decomposed; gasification was allowed to proceed under identical conditions used for the calcium oxide experiments. It was observed that after two hours, a 5% loading of potassium oxide gasified 85% of the Sphero carb compared to 60% for calcium oxide. Hence, it appears that potassium is a more efficient catalyst at this level of loading. No distinct potassium species could be identified by x-ray analysis of the gasified products; this would seem to indicate that the potassium oxide remains poorly crystallized during the entire gasification process.

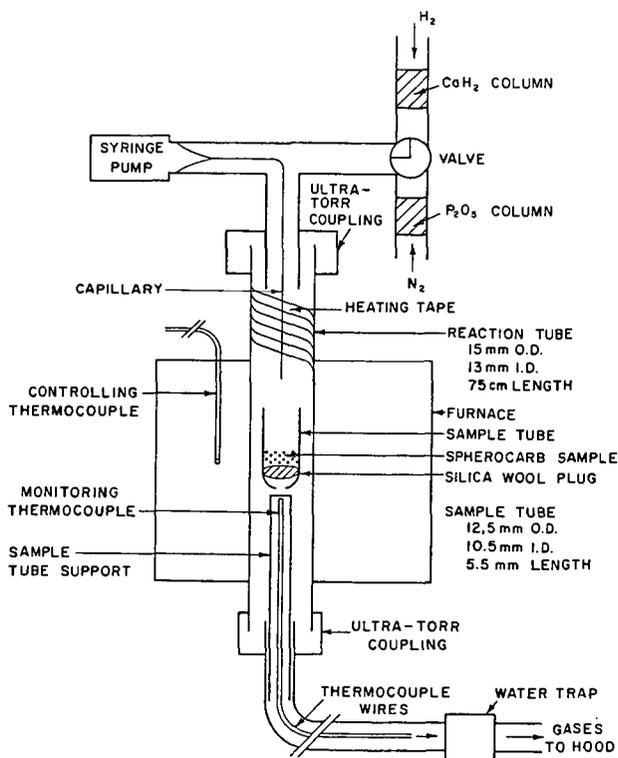
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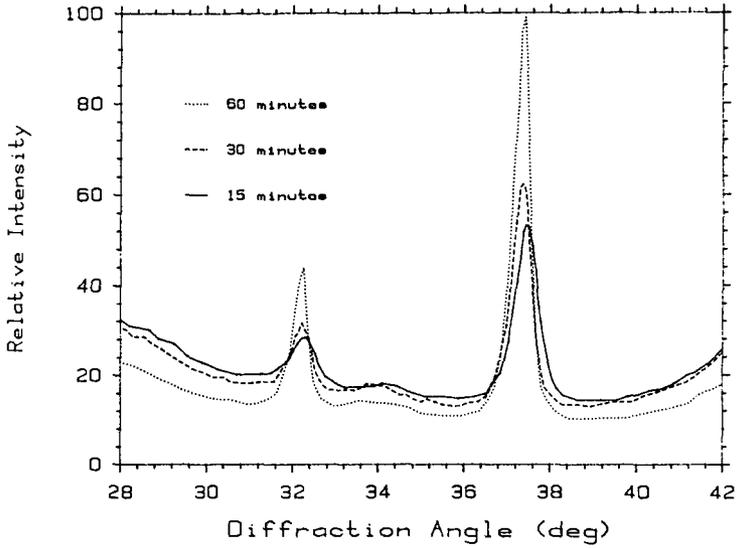
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CaO on Spherocharb



Gasification of Carbon

