Synthesis and study of carbon microspheres for use as catalyst support for cobalt


The production of pure carbon spheres was achieved in the absence of a catalyst through the direct pyrolysis of two hydrocarbon sources, acetylene and ethylene. Systematic studies using acetylene as the feedstock indicated that the size distribution of the resulting carbon microspheres can be controlled by pyrolysis temperature, time and feedstock flow rate. The resulting spheres were fully characterised by transmission electron microscopy (TEM) and thermogravimetric analysis. The TEM examination showed that these spheres have a ball-like and chain-like morphology, and the balls have smooth surfaces with a variation in diameter size and distribution determined by the reaction conditions. Carbon microsphere-supported cobalt catalysts were synthesised and have shown good activity in the ethylene hydrogenation reaction.

Key words: carbon microspheres, supports, ethylene hydrogenation, electron microscopy, cobalt

Introduction
Carbon is a versatile element because it can be a useful building block to form a wide range of structures. The unique ability of carbon to form complexes in which the carbon atom has sp, sp² and sp³ electronic configurations results in a wide range of structures and morphologies with widespread applications. The successful growth of diamond films, the fullerene molecule C₆₀ and its family members C₇₀ e.g. C₈₀ and C₉₀, and carbon nanotubes (CNTs) have attracted much attention. In particular, an enormous amount of research has to date focused on the synthesis and applications of CNTs. Another spherical form of carbon, which is graphitic in nature, has recently been emphasised in the literature. Earlier studies referred to this spherical material as nanosized carbon spheres or carbon nanobeads, while more recent studies have called them carbon spheres, nanoballs, carbon pearls or carbon microspheres. This form of carbon has not received as much interest to date by those working with CNTs because in most cases it was discovered accidentally as a byproduct in the synthesis of CNTs by chemical vapour deposition methods. However, since then, some work has been carried out on these carbon microspheres (CMSs), focusing on their fabrication using catalytic synthesis as well as direct pyrolysis of hydrocarbons. Interestingly, carbon spheres have been known for many decades and have been made by procedures similar to the methods described herein. These materials, referred to as carbon black particles, have been produced from a carbon source such as oil or natural gas, typically in the presence of small amounts of oxygen. For example, when acetylene is used under a reduced presence of oxygen the process is called the acetylene black process.

Different processes have been used to synthesise the sphere-like forms of carbon. Carbon onions were observed to be formed from soot that contained polyhedral carbon particles under electron-beam irradiation in a high-resolution transmission electron microscope. These highly graphitic structures were found to be stable under irradiation conditions. Monodispersed nanosized carbon spheres (~210 nm in diameter) were synthesised by Wang and Kang using a mixed-valent oxide catalytic carbonisation process in which methane was decomposed at 1100°C in the presence of a metal oxide catalyst. When a temperature of 950°C was used, carbon tubes were produced. Solid and hollow nanospheres with diameters in the range 250–850 nm have also been obtained by a catalytic process by Sharon et al. from camphor vapour at 1000°C using ferrocene as the catalyst precursor. All the above processes are reported to require a catalyst. More recently, large-scale production of pure carbon spheres, with diameters from 50 nm to 1 μm, has also been achieved through direct pyrolysis of a wide range of hydrocarbons in the absence of a catalyst. These include styrene, toluene, benzene, hexane, cyclohexane and ethane. Wang et al. have also reported the production of carbon microbeads (2 mm) from a synthetic naphthalene isotropic pitch by simple heating at 420°C under nitrogen.

In this study we report on the synthesis of CMSs, using ethylene or acetylene as a carbon source, in the absence of a catalyst.

The search for new synthetic strategies for generating nanostructured carbon or carbon-hybrid materials is topical in materials chemistry, motivated by the natural abundance of carbon and therefore the cost effectiveness of carbon precursors and the promising applications of the resulting materials. Due to the intrinsic properties of the carbon materials, such as their high strength, high thermal resistance and light weight, CMSs can be used as high-strength composites, catalyst supports, lubricants and as wear-resistant materials.

Catalytic hydrogenation is a common and straightforward application of a heterogeneous catalyst. The usefulness of this reaction has been well covered by texts and reviews. Such work, however, has been done on amorphous carbon as a catalyst support in hydrogenation reactions, and similar work on new forms of carbon, such as CMSs, remains to be explored. We recently reported that carbon microspheres could be used as a catalyst support for palladium (Pd) for the hydrogenation reaction of ethylene to ethane. The study showed that better ethylene hydrogenation activity and mechanical stability against deactivation were achieved when compared to an activated amorphous carbon-supported Pd catalyst. This was suggested to be due to the stronger metal-support interaction between the Pd and the carbon, even though some sintering was noted. The use of CMSs as support for cobalt (Co) catalysts for the hydrogenation reaction of ethylene to ethane, has not previously been reported and fewer sintering episodes are expected. Herein we report our results on the use of Co/CMS for the hydrogenation reaction of ethylene to ethane.

Methods
Carbon microsphere synthesis
Direct pyrolysis of a pure hydrocarbon source was carried out to synthesise carbon microspheres. The experiment was carried out at atmospheric pressure in a flow reactor made of a quartz tube (having dimensions 51 × 1.9 cm). The reactor was placed...
horizontally into an electronically-controlled furnace. The front 
end of the tube was connected to a glass manifold which allowed 
for the free flow of gases (i.e. hydrocarbon feedstock gas, argon 
inert gas) into the reactor. The rear end of the tube was closed 
with a quartz glass plug, thus ensuring that the reaction took 
place in the absence of oxygen.

The temperature in the furnace was then raised at a constant 
heating rate of 10°C min$^{-1}$ under a constant flow rate of 40 ml 
min$^{-1}$ of 5% H$_2$/Ar gas. Once the desired temperature was 
reached the inert gas was replaced with the hydrocarbon source 
(i.e. acetylene or ethylene) at a total constant flow rate of 100 ml 
min$^{-1}$. The carbon source was converted into the desired actu-
vated carbon species which diffused into the quartz tube while 
the temperature was held constant. After a certain time, the 
carbon source was replaced by the inert gas (5% H$_2$/Ar, 40 ml 
min$^{-1}$), and the system was allowed to cool to room temperature 
before the product was collected. The soot was collected, 
weighed and characterised using TEM (JEOL 100S Electron 
Microscope) and thermogravimetric analysis (TGA) (Perkin 
Elmer Pyris 1 TGA Analyzer). Since no catalyst was required in 
the synthesis of the CMSs, the materials produced were very 
pure and no removal of catalyst was required in the post-
synthesis process. The type of feedstock gas, reaction tempera-
ture, reaction time and flow rate of the carbon source were 
varied in order to study their effects on the structure and yield 
of CMSs obtained.

Preparation of carbon microsphere supported cobalt catalysts 
(Co/CMS)

The CMS supported Co catalysts were prepared by the wet 
impregnation method. Cobalt nitrate [Co(NO$_3$)$_2$·6H$_2$O] was used 
as a source of cobalt. For the synthesis of 5 g of 5 wt% Co/CMS, 
1.24 g of cobalt nitrate was dissolved in 20 ml distilled water and 
the solution stirred. Other catalysts containing 10 wt% and 
20 wt% Co were also prepared as described above. Each of the 
support-catalyst mixtures was stirred for 15 min and dried in an 
oven at 120°C for 30 min. The catalysts were then calcined in a 
static air calcination oven for 4 h at 400°C (heating rate = 5°C 
min$^{-1}$) and rapidly ground to a fine powder and sieved (powder 
< 150 µm). Temperature-programmed reduction (TPR) studies 
were done to determine the reduction temperature of cobalt 
oxide species under hydrogen and indicated that a temperature 
of 400°C would be sufficient for catalyst reduction (data not 
shown). The catalysts were then reduced under a continuous 
flow of 5% H$_2$/Ar at 30 ml min$^{-1}$ for 1 h.

Catalytic hydrogenation reaction

The catalytic hydrogenation reactions were performed, at 
atmospheric pressure, by passing a gaseous feed containing 
pure ethylene and hydrogen (H$_2$/C$_2$H$_4$ mol ratio = 3.05, total 
flow of feed gas = 77 ml min$^{-1}$) continuously over the catalyst 
(50 mg), which was packed in a fixed-bed quartz microreactor 
with a thermocouple. After attaining reaction steady state, the 
reaction products were analysed by a gas chromatograph with a 
flame ionisation detector (FID) using a Porapak Q column. The 
catalyst was studied in its prepared state. Only hydrocarbon 
products are detected by the FID and hence selectivity and con-
version data were based only on analysis of the hydrocarbon 
species. The gas hourly space velocity was measured at 0°C and 
1 atm pressure. The experimental setup is shown in Fig. 1.

Results and discussion

Effect of carbon source

The direct hydrocarbon pyrolysis experiments using acetylene 
and ethylene as the carbon source were performed over a wide 
temperature range (600–950°C). Ethylene gave no CMS forma-
tion at 600–850°C. Low yields were obtained at 900°C (0.2 g) 
while the maximum yield attainable was 1.4 g at 950°C and 
the CMSs formed had a broad size distribution range (350– 
650 nm).

With acetylene, CMSs were observed at all temperatures used 
and very high yields were obtained at 900°C (>10 g). The size 
distribution was also much narrower than that observed with 
ethylene. As a result, acetylene was used as the source of carbon 
to make CMSs in this study. It may be noted that the yields 
reported above and others to follow, relate to the mass of the 
carbonaceous materials observed in the products. Our method of carbon microsphere production 
resulted in the synthesis of a clean material with purity >99%, as 
determined by TEM analysis.

Effect of temperature

The effect of temperature on the yield, size and morphology of 
the carbon spheres was investigated. Experiments were carried

![Fig. 1. Experimental setup used for the catalytic ethylene pyrolysis reaction (GSV 2 = gas sampling valve, FCV = flow control valve).](image-url)
out in a temperature range of 600–1000°C. At each experimental temperature, the carbon deposit was removed from the reactor and weighed. Transmission electron microscopy studies of the products enabled the measurement of their diameters as well as their distribution. The acetylene gas flow rate was kept at 100 ml min⁻¹ and a reaction time of 2 h was used unless otherwise stated. The effect of temperature on the yield is represented graphically in Fig. 2.

The yield of CMSs produced when acetylene was the feedstock gas increased with temperature from 600°C (<0.2 g) to 900°C (>7.0 g). Thereafter, the yield decreased with further increase in temperature from 900°C to 1 000°C. After further experiments (not shown) we could conclude that the optimum temperature for the production of carbon microspheres under the reaction conditions was 900°C. The size and diameter distribution of the carbon spheres became larger with an increase in temperature as shown in Fig. 3. At 600°C, the average diameter of the spheres was 250 nm with uniform distribution (Fig. 3a). At 950°C (Fig. 3b) and 1 000°C (not shown), the average diameter size increased to 1 000 nm and 1 300 nm respectively, with a broader diameter distribution. The higher temperature produced a larger size CMS.

The diameter distribution of CMSs obtained at a temperature of 900°C with a C₂H₂ flow rate of 100 ml min⁻¹ is shown in Fig. 4. It can be seen that the diameters of carbon spheres obtained were in the range of 300–1 900 nm, with about 90% in the range of 800–1 000 nm. This implies that the carbon spheres obtained at 900°C were quite uniform in size.

**Effect of reaction time**

The acetylene pyrolysis time was varied from 5 min to 300 min at a set temperature. The yield of CMSs increased almost linearly with an increase in pyrolysis time (Fig. 5). The products however changed from being soft and powdery to hard solid products at reaction times >50 min. It appears that the hardness was related to a core-shell structure; with increased time in the hot reactor the shell formed, and this made the spheres ‘harder’.

A diameter distribution was observed within each sample that was studied under TEM. The observed variation of the diameters of the carbon microspheres within a unique experiment prompted the investigation of the effect of the temperature gradient inside the reactor. A series of experiments were thus performed at an acetylene flow rate of 100 ml min⁻¹, a pyrolysis time of 2 h and a temperature of 900°C (Fig. 6).

By analysing samples collected in the three different boats used in each experiment, it was observed that the microspheres in each boat contained material with uniform diameters. However, the boats contained different sizes of microspheres. Generally, the boat placed at the centre of the tube closest to the thermocouple i.e. boat 2, contained spheres with larger diameters (Fig. 7). This observation was attributed to the fact that the temperature in the reactor is highest at this point. These results agree with those obtained earlier, that showed that the diameters of the microspheres increased at higher temperatures. Multiple...
conglomerates of the carbon spheres were abundant in some cases, even with experiments conducted at a pyrolysis time of 5 min (Fig. 8).

Characterisation of CMSs

A growth mechanism for the graphitic CMSs has been proposed based on the microstructural information obtained by high resolution transmission electron microscopy (HRTEM). Our study is in agreement with previous studies and reveals that the carbon spheres are perfectly round, clean, solid and do not contain any large porosity (surface area 10 m$^2$ g$^{-1}$). The structure is composed of graphitic flakes and the flakes are in the size range of 1–30 nm, with a partial order similar to earlier reports. The flake-like nature of the CMSs implies that the surface structure is defective. This suggests that functionalisation of the spheres should be possible and that if metals are attached to the surface they should bind with ease. Indeed it is this feature that suggested that the Co/CMS materials should be excellent catalysts.

Thermogravimetric analysis was used to study the thermal stability of the carbon microspheres. The TGA profile was compared to that of carbon nanotubes (CNTs) that were synthesised in our laboratory. It was anticipated that if the spheres were graphitic, they should be stable up to about 600°C, after which they would begin to gradually lose weight in air to about 800°C. The TGA profiles are shown in Fig. 9. The differences observed between the two profiles are as shown. It may be noted that the TGA profile of the CNTs contained residual metal oxide (3%) associated with the catalyst used to make the CNTs. This can be contrasted with CMSs that contained only carbon and no deposit was left at temperatures greater than 800°C.

The effect of temperature on the performance of Co/CMS as a catalyst

The activity of as-synthesised (without any pre-treatment) as well as pre-reduced 5 wt%, 10 wt% and 20 wt% Co/CMS catalysts was investigated for the ethylene hydrogenation reaction. As expected, the unreduced catalysts were less active and no further information on these unreduced materials will be reported here. The order of activity for the reduced catalysts was 10 wt% > 20 wt% > 5 wt%. This effect relates to the exposed surface Co atoms and suggests that if the metal particles are too large, then catalytic activity is lowered. This issue will need to be explored further in later studies. The optimum temperature for the conversion of the ethylene was found to be 100°C for all three catalysts. The conversion of C$_2$H$_4$ with the 10 wt% Co/CMS catalyst was approximately 100% at 100°C. However, at higher temperatures (T > 100°C), the activity of all three catalysts decreased significantly (Fig. 10). This decrease could have arisen from catalyst deactivation by sintering or by deposition of carbonaceous deposits on the Co. The latter explanation is discussed below.

Time on stream studies using pre-reduced catalysts

The pre-reduced catalysts were tested for activity by running reactions for 16 h. The amount of C$_2$H$_4$ conversion was monitored at regular time intervals. It was observed that the catalysts maintained a markedly high percentage conversion throughout the reaction (Fig. 11). Such activity is not always observed with many commonly used hydrogenation catalysts (e.g. Pt, Pd and Ni), which are usually supported on silica, activated carbon and γ-alumina. The data suggest that sintering of the catalyst particles and poisoning due to coverage of the Co by carbonaceous material, are not taking place at this temperature. Further, it is believed that catalyst sintering is highly unlikely under these mild reaction conditions and preliminary HRTEM results suggest no change in catalyst particle size after reaction.

Conclusion

We have demonstrated that direct pyrolysis of C$_2$H$_2$ in the absence of a catalyst is an efficient method to produce carbon...
microspheres. Different pyrolysis conditions were used to study the size and morphology as well as the distribution of the resulting microspheres. The effect of pyrolysis temperature played an important role and influenced both the size and yield of the product. The experiments performed showed that at 900°C, the resulting spheres were prepared in high yield, were of large size (~1 µm) and had uniform distribution (not less than 90%). The detailed experiments conducted with C₆H₆ as a precursor indicate that the diameters of the carbon spheres can be controlled by varying the pyrolysis conditions (e.g. temperature and deposition time) and that the process could readily be scaled up for commercial production.

Carbon microspheres have shown to be a promising support for metal catalysts. The percentage of catalyst loading greatly affects the activity of the CMS-supported catalysts. The CMS-supported catalysts showed remarkable stable activity for a long period of time on stream. The abundance of defects in the CMS makes them highly reactive and is consistent with their catalytic support applications. The possibilities for further surface chemical modification of the CMSs to produce modified catalyst supports is to be explored.

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