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Catalytic growth of structured carbon from chloro-hydrocarbons

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Abstract

The catalytic growth of structured carbon from C_2H_4, C_2H_6, $C_2H_2Cl_2$, C_2HCl_3, $C_2H_4Cl_2$ and $C_2H_3Cl_3$ promoted by Ni/SiO$_2$ in the presence of H_2 over the range $673\ K \leq T \leq 1073\ K$ has been examined. The presence of Cl served to enhance carbon deposition where carbon yield (at $T < 850\ K$) increased in the order $C_2H_6 < C_2H_4 < C_2H_4Cl_2 < C_2H_3Cl_3 < C_2H_2Cl_2 \leq C_2HCl_3$; at $T > 900\ K$, carbon yield converged for $C_2H_3Cl_3$, $C_2H_2Cl_2$ and C_2HCl_3. Carbon efficiencies (fraction of carbon in the inlet feed that is converted to a solid carbon product) in excess of 96% have been achieved. Conversion of C_2H_4 also generated C_2H_6 (hydrogenation) as a secondary reaction while CH_4 (hydrogenolysis) production from C_2H_4 and C_2H_6 was observed where $T > 900\ K$. The chloro-hydrocarbon to carbon reaction generated HCl as the only inorganic product with no evidence of Cl_2 or chloro-organics in the product stream, *i.e.* Ni/SiO$_2$ solely promotes a composite dehydrochlorination/decomposition. The nature of the carbonaceous product has been characterized by a combination of TEM, SEM, XRD, BET area and temperature programmed oxidation (TPO). Carbon yield from C_2H_6 and C_2H_4 passed through apparent maxima at 773 and 993 K, respectively, and took the form of high aspect ratio graphitic nanofibres with a central hollow core and diameters in the range 5–180 nm. Carbon deposition from $C_2H_4Cl_2$, $C_2H_3Cl_3$ and $C_2H_2Cl_2$ increased with increasing temperature to deliver essentially a carbon yield invariance where $898\ K \leq T \leq 1023\ K$. The carbon fibres from the latter reactants exhibit a "segmented" or "bamboo-like" structure with diameters up to 560 nm. In complete contrast, catalytic decomposition of C_2HCl_3 resulted predominantly in nanosphere formation. These nanospheres exhibited a wide diameter range (35–680 nm) with a conglomeration or clustering and are characterized by a lesser structural (graphitic) order than the nanofibres produced from C_2H_4 and C_2H_6.

Keywords: Chloroethylene(s); Chloroethane(s); Ni/SiO$_2$; Catalytic decomposition; Carbon growth; Carbon nanofibres; Carbon nanospheres

1. Introduction

The discovery of structured carbon materials with nano-metre dimensions, *i.e.* fullerenes, nanotubes and nanofibres, has led to a renaissance in the study of carbon-based materials due to their unique chemical and physical properties that can be exploited in adsorption [1], H_2 storage [2] and electronics applications [3]. Moreover, the inherent mechanical properties can be used to good effect as additives for reinforcement [4] while metallic/semi-conducting properties can impact on conductivity [5] in various composites. Although there are many potential applications, widespread utilization requires a low cost means of fabrication that exhibits a high degree of control and reproducibility. Ordered carbon structures have been detected in benzene, acetylene and ethylene flames [6] but flame synthesis is not viewed as a viable preparative strategy. The direct synthesis of graphitic nanotubes and/or nanofibres is now well established by arc discharge and plasma decomposition [7] but such techniques also yield polyhedron carbon nanoparticles (low aspect ratio) and an appreciable amorphous component. This necessitates a cumbersome and costly purification stage, involving a combination of chemical treatment/ultrasound and selective oxidation and/or hydrogenation [8] in order to extract the desired structured product. These methodologies are highly energy demanding batch processes and the amount of material that can be produced is limited. Alternatively, a catalytic route can generate a carbon product with a high degree of uniformity in terms of dimensions, morphology and lattice structure while scale-up is far more feasible [9].

In general, catalytic synthesis involves the decomposition of a carbon-containing gas stream, typically diluted with an inert (He, Ar) and possibly reactive (H_2) gas flow. The yield and

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nature of the carbonaceous product is determined by the catalytic metal, the hydrocarbon source, reaction/contact time and temperature [10]. Carbon nanofibres, the subject of the authors' earlier work [11–17], are high aspect ratio structures, characterized by a series of ordered parallel graphene layers with an interlayer distance of *ca.* 0.34 nm. The exposed surface mainly consists of prismatic planes with high surface reactivity when compared with the basal planes of graphite. The growth of ordered carbon has been promoted by Ni as the catalytic agent, employed in both unsupported [18,19] and supported [20–23] forms. Carbon nanofibre synthesis has been recorded and characterized (to varying degrees) from a catalytic decomposition of CO [24–26] and a diversity of aliphatic [19–23,27–30] and, to a lesser extent, aromatic [17,31,32] feedstock. Hydrogen is not an essential component in these systems but its presence has been shown to be highly beneficial in initiating decomposition of the carbon-containing gas [33] and exerting additional structural control on the carbon growth [34]. We have shown that carbon nanofibre yield can be controlled through a judicious choice of catalyst and reaction conditions [13,15]. Variations in the nature of the support and Ni loading can induce differences in nanofibre diameter and morphology [10,16]. Fibre diameter is directly related to the starting metal particle size although there is evidence of metal sintering during reaction leading to wider fibres. Variations in fibre morphology are a direct consequence of Ni-support interactions [10,35]. Moreover, doping Ni/SiO_2 with Cl (or Br) was shown [10,13,16,36] to result in an increase in nanofibre yield as a result of electronic perturbations in the active Ni sites which favoured reactant decomposition. In this study, we examine further the role of Cl in determining structured carbon growth by considering the Ni/SiO_2 promoted decomposition of dichloro- and trichloro-ethane/ethylene, which is assessed against the conversion of ethane/ethylene. We focus on time-on-stream and temperature responses with a comprehensive characterization of the carbon product involving temperature programmed oxidation (TPO), BET area, XRD, TEM and SEM analyses.

2. Experimental

2.1. Catalyst preparation/activation and reaction

The Ni/SiO_2 catalyst was prepared by standard incipient wetness impregnation of SiO_2 (Sigma–Aldrich fumed silica) with an aqueous solution of $Ni(NO_3)_2$ to yield a 9.4% (w/w) Ni loading, determined by inductively coupled plasma-optical emission spectrometery (ICP-OES, Vista-PRO, Varian Inc.). The catalyst precursor was sieved (ATM fine test sieves) into a batch of 100 μm average particle diameter, loaded into a fixed bed tubular quartz reactor (i.d. = 1.25 cm) and activated by heating at 10 K min^{-1} in 60 cm^3 min^{-1} (Humonics Model 520 flow meter) dry H_2 (99.999%) to the ultimate reaction temperature (673–1073 K). The catalytic reactor and operating procedure have been described in detail elsewhere [15,35] but some features, pertinent to this study, are given below. The decomposition reactions were conducted *in situ* (after catalyst activation) with a co-current flow of reactant (C_2H_4, C_2H_6, $C_2H_2Cl_2$, C_2HCl_3, $C_2H_4Cl_2$ or $C_2H_3Cl_3$) in H_2 for up to 60 min on-stream with no significant back pressure/flow fluctuations. A Model 100 (kd Scientific) microprocessor controlled infusion pump was used to deliver the chlorinated feed (C_2H_6 and C_2H_4 was delivered *via* a Brooks mass flow controller) *via* a glass/teflon air-tight syringe and teflon line at a fixed calibrated flow rate, which was carried through the catalyst bed in a stream of dry H_2. Bed temperature (±1 K) was monitored continuously by means of a thermocouple inserted in the catalyst bed. The inlet C/Ni was maintained at 0.16 $g_C\, g_{Ni}^{-1}\, min^{-1}$ with a gas hourly space velocity (GHSV) = 1.6×10^4. Condensable reactor effluent was frozen in a liquid nitrogen trap and non-condensables were collected in FEP^{TM} gas sampling bags (Sigma–Aldrich) for subsequent off-line capillary GC analysis (Perkin-Elmer Auto System XL, flame ionization detector, DB-1 50 m × 0.20 mm i.d., 0.33 μm column (J&W Scientific)). A chlorine (HCl product in the case of the $C_2H_2Cl_2$, C_2HCl_3, $C_2H_4Cl_2$ and $C_2H_3Cl_3$ feed) mass balance was performed by passing the effluent gas through two gas scrubbers (1 M NaOH), monitoring continuously the pH change by means of a Hanna HI Programmable Printing pH Bench-Meter. The concentration of HCl generated was also measured by potentiometric analysis of the scrubbing solution using a Metrohm (Model 728) Autotitrys where $AgNO_3$ served as titrant with a combined Ag electrode. Each catalytic run was repeated up to six times and the catalytic data quoted in this paper represent average values: the solid carbon gravimetric yield was reproducible to within ±8%. After reduction or after catalysis, the catalyst bed was flushed for 1 h in a stream of He, cooled (in He) to room temperature and passivated in (40 cm^3 min^{-1}) 1% (v/v) O_2/He.

2.2. Catalyst/carbon characterization

The catalyst temperature programmed reduction (TPR) profile was determined using the commercial CHEM-BET 3000 (Quantachrome) unit and has been published elsewhere [32]. After TPR, the sample was swept with 20 cm^3 min^{-1} dry N_2 for 1 h, cooled to room temperature and subjected to H_2 chemisorption using a pulse (50 μl) titration procedure; H_2 uptake measurements were reproducible to better than ±4%. BET areas were recorded with a 30% (v/v) N_2/He flow; pure N_2 (99.9%) served as the internal standard. At least two cycles of N_2 adsorption–desorption in the flow mode were employed to determine total surface area using the standard single point method; reproducibility was within ±2%. Temperature programmed oxidation (TPO) profiles of the catalytically generated carbon were obtained from thoroughly washed, demineralised (in HNO_3) samples to avoid any contribution due to a catalyzed gasification of carbon by residual Ni [35]. A known mass of the demineralised sample was heated from room temperature to 1273 K at 8 K min^{-1} in a 5% (v/v) O_2/He mixture with on-line TCD analysis of the exhaust gas. These profiles were assessed against those generated for model activated carbon and graphite samples (Sigma–Aldrich) which had also been subjected to the same demineralisation treatment.