



## Growth of nitrogen-doped filamentous and spherical carbon over unsupported and Y zeolite supported nickel and cobalt catalysts

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### ABSTRACT

Unsupported and Y zeolite supported nickel and cobalt catalysts have been tested for the growth of nitrogen-doped structured carbon via the chemical vapour decomposition (CVD) of acetonitrile where  $550^{\circ}\text{C} \leq T \leq 1150^{\circ}\text{C}$ . A range of carbonaceous structures, including carbon filaments with different lattice structures and carbon nanospheres were obtained. The graphitic character of the carbon product has been evaluated by means of temperature-programmed oxidation (TPO) and XRD analyses, surface area and porosity measurements for both catalyst and carbon product are provided and structural/morphological features illustrated by scanning and transmission electron microscopy (SEM and TEM). Carbon yield and morphology were strongly dependent on reaction temperature, the nature of the active metal and the use of a support. Carbon yield increased with increasing temperature (up to  $1050^{\circ}\text{C}$ ) to give maximum values in the order  $\text{Ni} < \text{Co} < \text{Ni/Y} < \text{Co/Y}$ . The supported catalysts delivered significantly higher carbon yields (up to  $35 \text{ g}_{\text{carbon}}/\text{g}_{\text{metal}}$ ) and initiated carbon growth at temperatures up to  $300^{\circ}\text{C}$  lower than that observed for the bulk metals. Carbon generated over Ni/Y and Co/Y at  $750^{\circ}\text{C}$  took the form of high aspect ratio nanofibres where the arrangement of graphene layers exhibited a periodic variation at higher reaction temperatures to ultimately result in a predominant production of nanospheres at  $1150^{\circ}\text{C}$ , rather attributed to a thermal than a catalytic route. Based on TPO analyses, carbon grown from bulk and supported Ni showed a higher degree of structural order compared with the Co promoted growth. An increase in reaction temperature served to enhance graphitic character. XRD analyses were in all the cases consistent with a graphitic product. Elemental (CHN) analysis of the carbon product has revealed a nitrogen content of up to 5 mol%.

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### 1. Introduction

The discovery of structured carbonaceous materials, notably carbon nanotubes and nanofibres [1], with a diversity of unique physical and chemical properties has attracted a significant research effort largely focused on controlled synthesis and developing new applications in gas adsorption [2],  $\text{H}_2$  storage [3] and electronics [4]. In addition, structured carbon has been used as catalyst support [5] and as an electrochemical promoter in fuel cells [6]. Doping these carbonaceous structures with heteroatoms, such as nitrogen or boron, is an effective means of modifying surface and electronic properties [7,8]. Indeed, it has been established that the incorporation of nitrogen in nanotubes results in enhanced conductivity, polarity and basicity, while modifying surface hydrophilicity [9].

Arc discharge and laser ablation have been employed in the synthesis of structured carbon [10,11] but these methods also produce a significant quantity of undesired by-products, such as carbon soot, that necessitates additional purification steps. Moreover, the associated low yields and high energy requirements have served as the impetus for the development of more efficient carbon production processes. A catalytic route, often termed chemical vapour decomposition (CVD), has emerged as a lower cost option which exhibits a greater degree of control and a more feasible scale-up [12]. CVD synthesis is now established using transition metals, such as Fe, Co and Ni [13]. Baker and co-workers [14] and Toebe et al. [15] have reported carbon growth over supported and unsupported metals where catalyst performance depended on the nature of the metal, the support and the reactivity of the carbon-containing gas. The interaction of the metal with a support can play a critical role in determining both carbon structure and yield. There have been a number of published CVD studies [16,17] that employed metals supported on amorphous oxides, e.g., silica and alumina. Hernadi and co-workers [18] recorded the first application of microporous crystalline zeolites (Y and ZSM-5) as support material where they

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**Table 1**  
Metal content, BET surface area, porosity and surface acidity associated with the catalysts considered in this study

Sample	BET surface area (m <sup>2</sup> /g)	Ext. surface area (m <sup>2</sup> /g) <sup>a</sup>	Micropore volume (cm <sup>3</sup> /g)	Meso- and Macro-pore volume (cm <sup>3</sup> /g)	Acidity (mmol NH <sub>3</sub> /g)	Metal content (% w/w)
Parent Y zeolite	828	3 (<1%)	0.312	0.008	0.214	–
Ni/Y	512	42 (8%)	0.183	0.137	1.351	20
Co/Y	471	94 (20%)	0.145	0.175	1.088	20
Ni + Y <sup>b</sup>	3	3	–	–	–	20
Co + Y <sup>b</sup>	2	2	–	–	–	20

<sup>a</sup> Values in parenthesis represent the external surface area as a percentage with respect to the total.

<sup>b</sup> Values refer to the bulk metal.

noted certain advantages over silica, notably a more facile purification as zeolites dissolve more readily than silica in strong acids. The general consensus [12,15,16] to emerge is that the use of supported catalysts facilitates the formation of narrower carbon fibres/tubes. Yu and co-workers have, however, noted [19] that this is not universally true in that unsupported Fe can also promote the growth of uniformly narrow carbon tubes when employing less reactive carbon precursors.

Compounds which have served as reactants in CVD syntheses include CO [20], methane [21], acetylene [20] and ethylene [13] with decomposition temperatures in the range 400–700 °C. With a view to generating a nitrogen-containing carbonaceous product, such carbon precursors as pyridine [22], dimethylformamide [23], aniline [24] and acetonitrile [25] have been considered where nitrogen can be considered an “n-type” dopant with an extra elec-

tron for donation when replacing carbon in the graphitic matrix. As nitrogen-containing hydrocarbons are less reactive, reaction temperatures in the range 800–1000 °C are required [22–25]. In earlier work, we reported the growth of structured carbon via the decomposition of ethylene over Y zeolite supported Ni [26,27] and recorded reproducible yields of uniformly sized carbon nanofibres. This work has since been extended to consider carbon growth over bulk and Y zeolite supported Ni and Co, using acetonitrile as the carbon precursor. In this work, the effect of temperature, reaction time, the nature of the active metal and the role of zeolite as support on carbon yield are considered while carbon structural features (morphology, aspect ratio and graphitic nature) are characterised. In the present work we report an unexpected shift in the predominant carbon growth from filament to nanosphere formation, where thermal decomposition is proposed to control the growth of the latest rather than catalysis. The viability of incorporating nitrogen in the carbon product is also addressed.

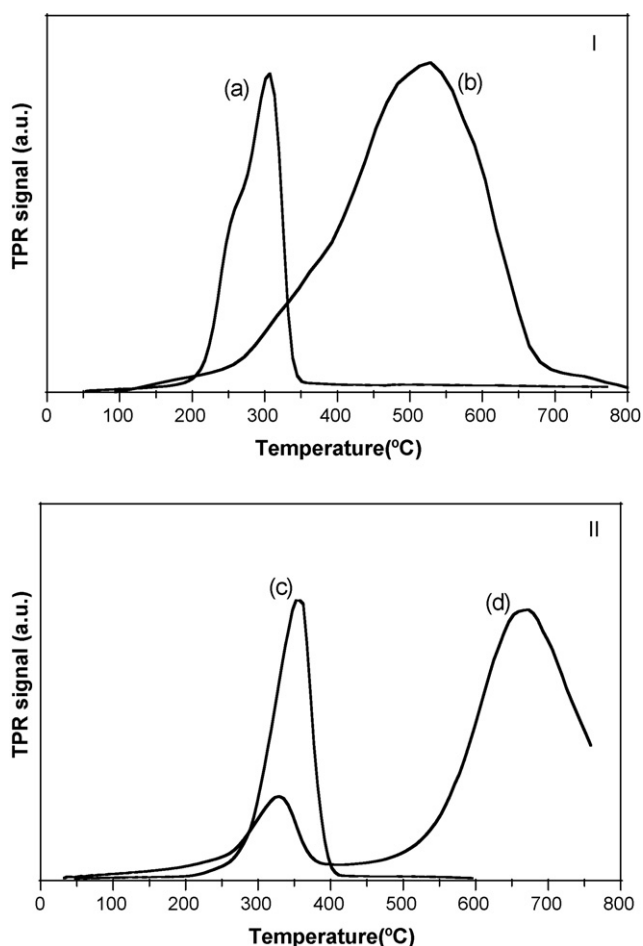
## 2. Experimental

### 2.1. Catalyst preparation

20% (w/w) Y zeolite (Zeolyst International) supported Ni and Co samples were prepared by homogeneous deposition–precipitation, as described in detail by Toebes et al. [15]. The as prepared catalyst precursors were filtered, thoroughly washed with deionised water and dried at 120 °C overnight. After drying, the catalysts were calcined in static air at 600 °C using a 10 °C min<sup>-1</sup> ramp and maintained at that temperature for 4 h. Before use, the catalyst precursors were sieved into a batch of 249 μm average particle diameter. Carbon growth was examined over Y zeolite supported and unsupported Co and Ni. In the latter case, commercial NiO (Aldrich) and Co<sub>3</sub>O<sub>4</sub> (Panreac) served as catalyst precursor in a physical mixture with the zeolite to achieve a 20% (w/w) metal content.

### 2.2. Catalytic synthesis of carbon nanostructures

Carbon growth was carried out at atmospheric pressure over the temperature range 550–1150 °C in a continuous flow fixed bed catalytic reactor (quartz tube, 3 cm i.d. × 60 cm) mounted in a temperature programmable oven. In each synthesis run, 200 mg of the catalyst precursor was reduced/activated by heating (10 °C min<sup>-1</sup>) in 100 cm<sup>3</sup> min<sup>-1</sup> dry 20% (v/v) H<sub>2</sub>/He to 600 °C, which was held for 1 h. The activated catalyst was thoroughly flushed in dry He for 1 h and subsequently brought to the ultimate reaction temperature before introducing the acetonitrile/He feed (GHSV = 16,000 h<sup>-1</sup>, 0.73 g<sub>C</sub> g<sub>metal</sub><sup>-1</sup> min<sup>-1</sup>). Carbon growth was monitored for up to 2 h on-stream: a reaction time of 1 h was taken as standard. The reactor was cooled to room temperature in a flow of He prior to off-line analyses. The specific carbon yields ( $Y_{\text{carbon}}$ ) reported in this paper represent the gravimetric ratio of solid carbon product to the metal



**Fig. 1.** TPR profiles generated for the reduction of I (a) Ni + Y, (b) Ni/Y and II (c) Co + Y and (d) Co/Y.

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