Chapter 2

Dechlorination

- Carbon tetrachloride
- Ethylene tetrachloride
- Copper powder
- Horn shaped Carbon nanotubes
- Hexachloro ethane
- Horn shaped Carbon nanotubes
- Carbon nanosheets
**Chapter 2: Synthesis of carbon nanomaterials using chloro-hydrocarbons as carbon source**

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Chapter 2: Synthesis of carbon nanomaterials using chloro-hydrocarbons as carbon source

2.1 Introduction

Since their discovery, carbon based nanostructures like carbon nanotubes (CNTs) [1] and fullerenes [2] have been extensively studied owing to their outstanding physical and chemical properties such as high mechanical strength [3], electrical conductivity [4] and thermal conductivity [5] etc. Due to their remarkable applications in various fields like energy storage [6], field emission devices [7], drug-delivery [8], catalyst support [9], semiconductor devices [10] and sensors [11], they have been attracting extensive attention of research community during the past decade. Various methods including arc-discharge [1], laser ablation [12] and chemical vapor deposition [13] have been proposed for the production of single-wall and multiwall CNTs. The physical properties of the CNTs usually depend on their structures. Different structure and morphologies of CNTs such as helix-, Y- and bamboo-shaped CNTs [14-16] have been reported. Among these, the horn shaped carbon nanotubes usually called carbon nanohorns (CNHs) [17] is one of the most attractive forms of CNTs. The CNHs are round-shaped aggregates of graphitic tubes with corn-shaped cap having a cone angle of 20° at one end, and these aggregates have a homogeneous diameter of 80–100 nm. Furthermore, CNHs form a unique nanostructure assembly with a "Dahlia-flower"-like feature. Typically, CNHs with high purity are produced by the CO₂ laser ablation of pure graphite under argon atmosphere in the absence of any metallic additives [17].

Carbon nanosheet (CNS) is a two-dimensional carbon nanostructure of stacked graphene sheets with few nanometer thicknesses [18, 19]. CNS is one of the interesting material in the carbon family due to its potential applicability in various fields such as gas storage [20], catalyst support [21], nano-electronics [22], electrode [23] and adsorption [24] etc. The chemical vapor deposition (CVD) based synthesis method has been well elaborated for the synthesis of CNS [25, 26] whereas different synthesis methods such as close-packing assembly [27], carbonization [28], catalytic thermal pyrolysis [29] and template-like method [30] have also been reported. Most of the synthesis methods of CNS include the use of graphite as a carbon source [31]. Very few methods utilized other carbon sources for the synthesis of graphene like
CNS but the use of the advanced techniques and low yield are the major disadvantages associated with it. Ando et al. [32] have reported the synthesis of petal-like graphite sheets using hydrogen arc discharge.

Dechlorination or reduction of chlorohydrocarbons using transition or alkali metal catalysts under mild solvothermal conditions is the one of promising and easy route for the synthesis of different carbon nanostructures [33]. Qian et al. [34] and Xiong et al. [35] synthesized CNTs with claw-like end and carbon hollow spheres with dechlorination of halocarbon using metal as reducing agent respectively. Besides, catalytic solid-state metathesis pathway has also been employed to prepare multiwall CNTs using chloride containing polymers, such as polyvinyl chloride and Li2C2 [36] as carbon source. Similarly, Kuang et al. [37] reported the low temperature solvothermal synthesis of crumpled CNS using metallic potassium and methane tetrachloride at 60 °C. Synthesis of nitrogen-doped horn-shaped carbon nanotubes (HSCNT) with carbon nanospheres as co-product has been reported by Wu et al. using pentachloropyrididine and metallic sodium [38].

The emission of carbon dioxide (CO2) from the industrial exhaust and burning of fossil fuel has been identified as a major contributor to global warming and climate change [39, 40]. Separation of particular gas up to a desired purity from various gas mixtures is an important process for economic and environmental reasons. Separation of CO2 from flue gas of thermal power plant or boilers which mainly contains the mixture of carbon dioxide and nitrogen along with minor percentage of moisture and other gases like SOx and NOx need the adsorbent material possessing high selectivity and adsorption capacity for CO2. The carbon monoxide with purity greater than 99% provides as a good feedstock for the chemical industry. Recovery of carbon monoxide from syngas by cryogenic processing is difficult, due to the very similar boiling points of carbon monoxide and nitrogen. Likewise, Recovery of CO from tail gas stream of ammonia plant which contains methane as major component, hydrogen and nitrogen as minor component is also difficult. Zeolite and activated carbon are the well-known commercially utilized adsorbent for the gas storage and separation [41-43]. Clay [44], metal organic framework [45] and porous silica materials [46] have been developed and studied as adsorbents for the CO2 sequestration. The adsorption capacity as well as
selectivity decides the applicability of the adsorbent in the separation and recovery processes.

In this chapter, we described the dechlorination pathway for the synthesis of HSCNTs and few layered functionalized CNS (FCNS) using different chloro-hydrocarbons as carbon sources and copper as reducing agent. The obtained product is also studied as the adsorbent for the carbon dioxide, carbon monoxide, methane and nitrogen gas adsorption at different temperatures up to 113 kPa pressure.
2.2 A solvothermal-reduction method for the production of horn shaped carbon nanotubes

2.2.1 Experimental

2.2.1.1 Synthesis of HSCNTs

In a typical experiment, metallic copper powder (19.73 g, 99.7% pure), CuCl₂·2H₂O (1.70 g, 99% pure) and CCl₄ (25 mL, 99.8% pure) were charged into Teflon-lined stainless steel autoclave of 75 mL capacity and was kept at 200 °C for 2 h in a preheated oven. After the reaction, the autoclave was allowed to cool to room temperature. The resultant hard and black solids were carefully collected and treated with 6 M HNO₃, followed by filtration and washing the residues with distilled water until the filtrate reaches neutral pH. Finally, the solid mass was air dried at 65 °C for 10 h. 1.45 g of product was obtained with chemical purity of ~99%. The yield of product on the basis of carbon content with respect to the metallic copper taken was ~43.5%.

2.2.1.2 Characterization of HSCNTs

The morphology and particle size of the samples were investigated by scanning electron microscopy (SEM, Leo 1430) and transmission electron microscopy (TEM) with a JEOL JEM-2100 TEM using an accelerating voltage of 20 and 200 kV respectively. The elemental composition of the sample was determined by Energy dispersive X-ray analysis (EDX) assembled with SEM and by CHN/S analyzer (Perkin-Elmer, Series II, 2400). The phase and crystallography of the product was investigated by powder X-ray diffraction (XRD) analysis with Philips X'Pert MPD system using PW3123/00 Ni-filtered Cu-Kα₁ radiation with slow scanning of 0.05°/s over the 2θ range 2°<2θ<80°. The Raman spectra of the samples were recorded on a Spex 1403 Raman spectrophotometer at ambient temperature, employing an argon ion laser at an excitation wavelength of 514.5 nm. DRIFT spectroscopy was performed at different activation temperature in nitrogen atmosphere using Perkins Elmer Spectrum GX 2500 FT-IR spectrophotometer, equipped with ‘The Selector’ DRIFT accessory (Graseby Specac, P/N 19900 series). The textural properties of the samples were evaluated using nitrogen adsorption-desorption measurements at 77 K with a volumetric system ASAP 2020.
Thermo gravimetric analysis (TGA) was done on Mettler Toledo TGA/SDTA 851 equipment under nitrogen flow (50 mL/min), at a heating rate of 10 °C/min. The surface functionality of HSCN was determined with infrared spectroscopy using Perkins Elmer Spectrum GX 2500 FT-IR spectrophotometer.

2.2.2 Results and discussion

![Fig. 2.2.1 XRD patterns of HSCNTs synthesized at 200 °C for 2 h (a) before and (b) after acid washing](image)

The XRD pattern of hard and black solids before acid wash (Fig. 2.2.1a) could be indexed to copper chloride hydroxide planes (JCPDS Card Files, No. 018-0439) present initially as a promoter and also formed as by-product. The XRD pattern of the product after acid treatment (Fig. 2.2.1b) showed broad diffraction peaks in the 2θ range 20–30° instead of comparatively sharp peak for typical graphitic planes at 2θ = 26.5° (JCPDS 41-1487) which reveals the amorphous nature of HSCNTs. The low crystallinity observed in the product may be due to the lower reaction temperature, not sufficient for the formation of self-assembly of graphitic carbon. Normally, amorphous carbon can be generated at low temperature, whereas graphitization can proceed at higher temperatures [47].

Raman spectroscopy is a very useful characterization tool for carbon materials. Mainly two Raman modes are observed at 1582 (G-band) and 42 cm⁻¹ (the shear mode of two adjacent sheets) for a single crystal of graphite [48]. In disordered carbons, new band (D-band) appears at ~1360 cm⁻¹ instead of the shear mode and the G-band becomes broad and is shifted to as far as 1600 cm⁻¹ (depending on the type
of material and the degree of disorder). A typical Raman spectrum (Fig. 2.2.2) of the sample shows the presence of the D- and G-bands, located at 1341 and 1578 cm$^{-1}$, respectively. The broadening of the bands is attributed to the amorphous character due to the post-treatment of HNO$_3$ required for isolation of product [49]. The D-band is intense and wide, and the estimated $I_D/I_G$ was 0.72, confirming that, as observed before by XRD, the obtained HSCNTs are substantially disordered. The Raman spectrum of obtained HSCNTs is slightly different than that of CHNs which may be due to the disordered structure of HSCNTs and the presence of amorphous carbon [50].

![Raman spectra of HSCNTs synthesized at 200 °C for 2 h](image)

**Fig. 2.2.2** Raman spectra of HSCNTs synthesized at 200 °C for 2 h

![SEM images representing (a) formation, (b) agglomeration of HSCNTs and (c) carbon material with fish-bone like morphology](image)

**Fig. 2.2.3** SEM images representing (a) formation, (b) agglomeration of HSCNTs and (c) carbon material with fish-bone like morphology
Chapter 2  Synthesis of carbon nanomaterials using chloro-hydrocarbons as carbon source

Fig. 2.2.4 TEM images showing (a) individual and (b) formation of HSCNTs and (c) HRTEM image shows HSCNTs are multiwall in nature

Fig. 2.2.3a and 2.2.3b display the SEM photographs of HSCNTs showing its formation and agglomerated form, respectively. From Figs. 2.2.3a and 2.2.3b, it is evident that the prepared HSCNTs are not in the form of spherical aggregates or dahlia-like structure, obtained by CO$_2$ laser ablation method used for production of CNHs [17]. The EDX analysis (not shown) of HSCNTs indicated the presence of carbon (70%), chlorine (17%) and oxygen (13%) on atomic basis. The TEM image of the individual HMWCNT (Fig. 2.2.4a) showed that the HSCNTs are about 1 μm in length with a well-defined uniform hollow core having the tube diameter of about 100 nm. Fig. 2.2.4b shows the growth of HSCNTs from the carbon surface. The HSCNTs are multiwall and disordered in nature having wall thickness of ~10 nm (Fig. 2.2.4c). The TEM analysis shows that the obtained HSCNTs are larger in all dimensions like length, diameter and wall thickness as compared to reported CNHs, and spherical aggregates or dahlia-like structure was not observed. The obtained HSCNTs are similar in shape with well-known CNHs but very much different in size, aggregation form, as well as Raman spectrum.

A broad band in DRIFT spectra at around 3400 cm$^{-1}$ at 25 °C (Fig. 2.2.5a) attributed to the O─H stretching mode of hydroxyl groups and adsorbed water which disappeared on heating to 150 °C due to the loss of adsorbed water. A peak at about 3350 cm$^{-1}$ (Fig. 2.2.5b – h) was due to the O─H stretching mode of carboxylic group and a band at 2929 cm$^{-1}$ due to C─H stretching. Their relative intensities decreased significantly as the activation temperature increased from 150 to 450 °C. A strong peak at ~1718 cm$^{-1}$ attributed to C═O stretching vibrations of carbonyl and/or carboxyl groups. The intense bands between 2400 and 2300 cm$^{-1}$ is assigned to adsorbed CO$_2$ molecules. The DRIFT analysis shows the presence of oxygen-
containing functional groups at the defect sites which might have formed during acid treatment [51].

![DRIFT spectra of HSCNTs at various temperatures in N2 atmosphere](image)

**Fig. 2.2.5** DRIFT spectra of HSCNTs at various temperatures in N2 atmosphere: (a) 25 °C; (b) 150 °C, t = 0 min; (c) 250 °C, t = 0 min; (d) 250 °C, t = 10 min; (e) 350 °C, t = 0 min; (f) 350 °C, t = 10 min; (g) 450 °C, t = 0 min; (h) 450 °C, t = 10 min

![Nitrogen adsorption-desorption isotherms and pore size distribution](image)

**Fig. 2.2.6** (a) Nitrogen adsorption-desorption isotherms at 77 K and (b) pore size distribution of HSCNTs calculated from the adsorption branch of the nitrogen isotherm by the BJH method

The N2 adsorption-desorption isotherm measurement provide information on the specific surface area and porosity of the resulting HSCNTs. Figs. 2.2.6a and b shows the N2 adsorption-desorption isotherms at 77 K and pore size distribution curve of HSCNTs from the adsorption branch of nitrogen isotherm by BJH model, respectively. The measured isotherm is found to be of Type IIb, generally obtained for aggregated powders which possess non-rigid slit-shaped pores. The relative
texture information is summarized in Table 2.2.1. However, some micro porosity was also observed in the sample may be formed during the acid treatment [49].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
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</thead>
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<tr>
<td></td>
<td>S_BET^a S_micro^b S_ext^c</td>
<td>V_T^d V_micro^e</td>
<td>D_BET^f D_BJH^g</td>
</tr>
<tr>
<td>HSCNTs</td>
<td>522.9 192.8 330.1</td>
<td>0.757 0.087</td>
<td>5.8 19.6</td>
</tr>
</tbody>
</table>

^aBrunauer-Emmer-Teller (BET) surface area; ^bMicropore surface area, calculated using t-plot method; ^cExternal surface area, calculated using t-plot method; ^dSingle point adsorption total pore volume, obtained at P/P₀ = 0.9710; ^ePlot micropore volume; ^fAdsorption average pore diameter, obtained from 4V/A by BET; ^gAverage pore diameter derived from adsorption branch of isotherm and BJH model.

Ostensibly, different reaction parameters played a crucial role in influencing the morphologies of carbon nanomaterials during their synthesis [52, 53]. In order to understand the role of reaction time and temperature during the formation, the reactions were carried out at 200 °C for 1 h and 150 °C for 2 h respectively, keeping all other parameters same. In both the experiments, product showed the fish-bone like morphology (Fig. 2.2.3c) having low carbon content (59% atomic basis) as compared to carbon content in HSCNTs (70% atomic basis) when the reaction was carried out at 200 °C for 2 h. Evidently, the formation of HSCNTs is time and temperature dependent. The formation of HSCNTs proceeded through an intermediate morphology that could be isolated from incomplete reactions. Insufficient reaction time or temperature resulted in fish-bone like morphology. The experimental data suggested that the growth mechanism of the HSCNTs is moderately similar to the Y-shaped carbon nanotubes in which branching is initiated by attachment of catalyst particle onto the side of growing carbon nanotubes [54]. The schematic representation of proposed growth mechanism for the formation of HSCNTs is depicted in Fig. 2.2.7.
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![Diagram of growth mechanism](image)

**Fig. 2.2.7** Schematic representation of proposed growth mechanism for the formation of HSCNTs: (a) Cu metal particles, (b) graphitic cluster formed on the Cu metal particles, (c) growth of tubular carbon structure with attached Cu particles on surface, (d) fish-bone like carbon structure and (e) HSCNTs

The temperature dependent growth rate of carbon nanomaterials could be influenced by several factors, including carbon concentration, diffusion rate of carbons and the rate of formation of carbon self-assembly [55]. It is generally agreed that the diffusion rate of carbon is the rate-determining step in the growth of carbon nanomaterials [56]. However, due to the low reaction temperature, the diffusion rate of carbon can be low, therefore, the carbon cluster mainly formed on the Cu metal particles as shown in Fig. 2.2.7b. The driving force of carbon to move away from the metal particle might be responsible for the tube like structure (Fig. 2.2.7c). The growth of one tube on the surface of other one is mainly due to Cu metal particles attachment onto the side of the carbon surface which results into the fish-bone like carbon structure (Fig. 2.2.7d) as an intermediate morphology. Finally, fish-bone like carbon material transformed into HSCNTs due to the stress (Fig. 2.2.7e).

### 2.2.3 Conclusion

Horn shaped multi-wall carbon nanotubes with uniform diameter of ~100 nm, an average wall thickness of 10 nm and length of about 1 μm were prepared using a solvothermal - reduction method employing carbon tetrachloride as a carbon source and metallic copper as reducing agent. The nitrogen sorption study showed that the obtained horn shaped carbon nanotubes possess the high surface area with different surface functionality as characterized by diffuse reflectance infrared Fourier transform spectroscopy. The detail experimental study showed that the growth of horn shaped carbon nanotubes was time and temperature dependent with fish-bone like morphology as intermediate structure.
2.3 A dechlorination pathway for synthesis of horn shaped carbon nanotubes using tetrachloroethylene as carbon source and its adsorption properties for CO₂, CH₄, CO and N₂

2.3.1. Experimental

2.3.1.1 Synthesis of HSCNTs

Synthesis of HSCNTs was carried in 40 mL Teflon lined autoclave containing metallic copper powder (10.0 g) and tetrachloroethylene (25.0 ml), heated at 200 ºC for 5 h in preheated oven. The black and hard solid product was filtered, crushed and stirred in 200 ml of 50% (V/V) of HNO₃ solution for overnight. Finally, the product was filtered and washed with plenty of distilled water so as to remove acid and metal ions followed by drying at 105 ºC for overnight.

2.3.1.2 Characterization of HSCNTs

The characterizations of obtained products were performed as described earlier in section 2.2.1.2.

2.3.1.3 Equilibrium gas adsorption study

The adsorption of CO₂, CH₄, CO and N₂ on HSCNTs was carried out with volumetric gas adsorption system (ASAP 2020, Micromeritics Inc., USA) up to 113 kPa pressure. The sample was activated in situ by increasing the temperature at a heating rate of 10 K min⁻¹ up to 573 K under vacuum (5×10⁻³ mmHg) and maintained for 5 h before the sorption measurements. The adsorption temperature was maintaining (± 0.1 K) by circulating water from a constant temperature bath (Julabo F25, Germany). The adsorption data were fitted into the Virial equation (Eq. 2.3.1), the obtained value of first Virial coefficient (A) was further used for the calculation of Henry's constant with the help of Eq. 2.3.2 [41].

\[
\ln \frac{p}{q} = A + Bq + Cq^2 + \cdots \tag{Eq. 2.3.1}
\]

where q is the amount of gas adsorbed per unit mass of the adsorbent, p is the equilibrium pressure; A, B and C are the first, second and third Virial coefficients respectively.

Henry’s constant:
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\[ K = \exp(-A) \quad \text{Eq. 2.3.2} \]

The capacity selectivity \( (S_{cap}) \) of gas 1 over gas 2 at particular pressure and temperature was calculated using Eq. 2.3.3 \[44\].

\[ S_{cap} = \frac{q_1}{q_2} \left( P, T \right) \quad \text{Eq. 2.3.3} \]

where \( q_1 \) and \( q_2 \) are the quantity of gas 1 and 2 respectively, adsorbed at a given pressure (P) and temperature (T).

The equilibrium selectivity \( (S_{eq}) \) between adsorbate at particular temperature was determined using the Henry’s constant as follows (Eq. 2.3.4) \[57\].

\[ S_{eq} = \frac{K_1}{K_2} \left( T \right) \quad \text{Eq. 2.3.4} \]

where \( K_1 \) and \( K_2 \) are the Henry’s constant for adsorbate 1 and 2 at particular temperature respectively.

Isosteric heat of adsorption was calculated with the help of software provided with surface area and pore size analyzer (ASAP 2020, Micromeritics Inc., USA) by fitting the adsorption data at 288 K, 303 K and 318 K in to Clausius-Clapeyron equation (Eq. 2.3.5).

\[ -\Delta H = R[\delta \ln P/\delta (1/T)]_\theta \quad \text{Eq. 2.3.5} \]

where \( R \) is the gas constant, \( P \) is the equilibrium pressure at the particular coverage \( \theta \) and \( T \) is the temperature in degree Kelvin.

2.3.2 Results and discussion

2.3.2.1 Synthesis of HSCNTs

Most of the synthesis methods of carbon nanomaterials involved the metal assisted reduction wherein the reduction of carbon source to elemental carbon by metal takes place. Dechlorination of chlorohydrocarbons by different metals under solvothermal condition is the versatile approach for the synthesis of various forms of carbon nanostructures. Scheme 2.3.1 represents the dechlorination pathway for the formation of HSCNTs.

\[ 2 \text{Cu} + \text{C}_2\text{Cl}_4 \xrightarrow{200^\circ\text{C}} 2 \text{C} + 2 \text{CuCl}_2 \quad \text{Scheme 2.3.1} \]
The morphological identification of product by SEM showed the formation of HSCNTs (Fig. 2.3.1). Fig. 2.3.1a shows the agglomerated forms of HSCNTs along with fish bone type carbon material, whereas Fig. 2.3.1b presents the individual form of HSCNT where one end of carbon nanotube is opened and other end is closed with the formation of cone shape. The product obtained from the present methodology also includes the fish-bone like carbon materials (Fig. 2.3.1c), an intermediate morphology during the synthesis of HSCNTs as described in section 2.2. The TEM image (Fig. 2.3.2a) has further confirmed the hollow nature of carbon nanotubes, open at one end and hemi circular at other end with wall thickness of ~50 nm (Fig. 2.3.2b). TEM images also showed that the obtained carbon nanotubes are not well crystalline and have irregular wall structure.

**Fig. 2.3.1** SEM images of (a) HSCNTs along with fish bone type carbon material, (b) separated single HSCNT, (c) carbon material with fish bone like morphology, (d) product obtained using higher amount of catalyst; (Table 2.3.3, Entry 8) (e) product obtained using lower volume of solvent; (Table 2.3.3, Entry 9) and (f) HSCNTs prepared using recovered tetrachloroethylene; (Table 2.3.3, Entry 10)
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Fig. 2.3.2 TEM images of (a) HSCNT and (b) wall of HSCNT having ~50 nm thickness

Fig. 2.3.3 (a) XRD pattern and (b) FT-IR spectrum of HSCNTs prepared using solvothermal dechlorination pathway

The amorphous nature of HSCNTs was indicated by XRD analysis (Fig. 2.3.3a), gave the broad diffraction peak having maximum intensity in the 2θ range of 25 - 27° typical for graphitic carbon planes at 2θ=26.5° (JCPDS 41-1487). The poor crystalline or amorphous nature of the carbon produced may be due to the low reaction temperature and acid treatment during the extraction of carbon product. The acid treatment and lower reaction temperature also results in to the affluent surface functionality on the surface of HSCNTs. The IR spectra of HSCNTs (Fig. 2.3.3b) shows the characteristic bands of hydrogen bonded –OH at 3437 cm⁻¹ for stretching and at 1383 cm⁻¹ for bending vibrations. The vibration band at 1619 cm⁻¹ corresponds to the presence of C= C groups. The weak transmission band at ~2850-2950 cm⁻¹ can be attributed to the stretching mode of –C–H bond indicating that C–
H groups are very scarce, due to the absence of hydrogen in carbon precursor and might have been created due to the acid treatment. The presence of surface chlorine atoms was detected by EDX analysis and is in the form of surface C–Cl bond confirmed by the presence of IR band at 753 cm$^{-1}$.

Fig. 2.3.4 (a) TGA and (b) DTGA plot of HSCNTs recorded under nitrogen atmosphere

Thermal analysis of prepared HSCNTs was carried out to examine its thermal stability (Fig. 2.3.4) and the obtained thermal profile was elaborated with respect to the elemental composition and availability of functional groups. The fading of adsorbed moisture was observed at $< 110 \, ^\circ C$ (1%, weight loss). In the temperature range of 110 – 300 $^\circ C$, total weight loss of 11% was observed mainly due to the physically adsorbed water as well as the decomposition of surface chlorine groups. The major weight loss (14%) in the region of 450 to 650 $^\circ C$ was observed due to the loss of oxygen containing surface functionality including –OH, –COOH, –CO– and –COO– etc [58].

The specific surface area (Table 2.3.1) of HSCNTs was determined using nitrogen sorption isotherm at 77 K (Fig. 2.3.5). The measured isotherm is of Type IIb and resembles with that of HSCNTs obtained from carbon tetrachloride (section 2.2), generally obtained for aggregated powders which possess non-rigid slit-shaped pores. The pore size distribution (inset of Fig. 2.3.5) of HSCNTs determined using desorption branch of the nitrogen isotherm by BJH model showed the presence of pores in the range of 2 to 5 nm contributing to the major part of pore volume due to
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the mesoporous characteristics of HSCNTs. The elemental composition of HSCNTs is given in Table 2.3.2.

**Table 2.3.1** Specific surface areas, specific pore volumes and average pore size of HSCNTs

<table>
<thead>
<tr>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{BET}}^a$</td>
<td>$S_{\text{micro}}^b$</td>
<td>$S_{\text{ext}}^c$</td>
</tr>
<tr>
<td>728.6</td>
<td>268.8</td>
<td>459.8</td>
</tr>
</tbody>
</table>

*Mathematically, the value of these parameters are as follows: $S_{\text{BET}}$ **Brunauer-Emmer-Teller (BET)** surface area; $S_{\text{micro}}$ **Micropore surface area**, calculated using t-plot method; $S_{\text{ext}}$ **External surface area**, calculated using t-plot method; $V_T$ **Single point adsorption total pore volume**, obtained at $P/P_0 = 0.9730$; $V_{\text{micro}}$ **t-Plot micro pore volume**; $D_{\text{BET}}$ **Adsorption average pore diameter**, obtained from $4V/A$ by BET; $D_{\text{BJH}}$ **BJH desorption average pore width**

**Fig. 2.3.5** Nitrogen adsorption and desorption isotherm of HSCNTs at 77.7 K and pore size distribution (inset) determined with desorption branch of the nitrogen isotherm by BJH model

**Table 2.3.2** Elemental composition of HSCNTs

<table>
<thead>
<tr>
<th>Elements</th>
<th>CHN/S analysis</th>
<th>EDX analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight%</td>
<td>Weight%</td>
</tr>
<tr>
<td>Carbon</td>
<td>69.4</td>
<td>67.1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>26.3</td>
<td>24.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Copper</td>
<td>---</td>
<td>1.4</td>
</tr>
<tr>
<td>Chlorine</td>
<td>---</td>
<td>6.7</td>
</tr>
</tbody>
</table>

*This table lists the elemental composition of HSCNTs as measured by CHN/S analysis and EDX analysis.*
2.3.2.1.1 Effect of reaction temperature and time

The effect of reaction temperature and reaction time on the product formation was examined by carrying out the reactions at different temperatures with variable time (Table 2.3.3). No product formation was observed when the reaction carried out at 150 °C for 24 h, whereas the reaction at 300 °C for 24 h produced very hard product which required harsh treatment of nitric acid to recover the carbon materials, and the obtained morphology shows the breakage of carbon tubes (Fig. 2.3.1d) may be due to the effect of high reaction temperature in combination with harsh post treatment of nitric acid.

The effect of reaction time studied from 2 to 24 h at 200 °C revealed that the reaction did not proceed in 2 h. Moreover if the reaction is carried out for more than 5 h i.e. for 12 and 24 h, there was no effect on the yield as well as carbon structure.
### Table 2.3.3 Optimization of reaction parameters for the synthesis of HSCNTs using Copper metal as catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Carbon source: Tetrachloroethylene (mL)</th>
<th>Catalyst Copper (g)</th>
<th>Reaction temperature (°C)</th>
<th>Reaction time (h)</th>
<th>Yield (g)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Effect of reaction temperature</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>10</td>
<td>150</td>
<td>24</td>
<td>---</td>
<td>No product formation</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>10</td>
<td>200</td>
<td>24</td>
<td>0.68</td>
<td>Recovered solvent, 20 mL</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>10</td>
<td>300</td>
<td>24</td>
<td>---</td>
<td>Reaction carried out in SS reactor, Very hard product obtained (difficult to isolate)</td>
</tr>
<tr>
<td><strong>Effect of reaction time</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>10</td>
<td>200</td>
<td>12</td>
<td>0.63</td>
<td>Recovered solvent, 20 mL</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>10</td>
<td>200</td>
<td>5</td>
<td>0.67</td>
<td>Recovered solvent, 20 mL</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>10</td>
<td>200</td>
<td>2</td>
<td>---</td>
<td>No product formation</td>
</tr>
<tr>
<td><strong>Effect of catalyst amount</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>5</td>
<td>200</td>
<td>5</td>
<td>0.27</td>
<td>Recovered solvent, 20 mL</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>20</td>
<td>200</td>
<td>5</td>
<td>1.24</td>
<td>Recovered solvent, 15 mL</td>
</tr>
<tr>
<td><strong>Effect of carbon source volume (autogenous pressure)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>10</td>
<td>200</td>
<td>5</td>
<td>0.72</td>
<td>---</td>
</tr>
<tr>
<td><strong>Reusability of carbon source</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Recovered 1st time, 25</td>
<td>10</td>
<td>200</td>
<td>5</td>
<td>0.35</td>
<td>Recovered solvent, 20 mL</td>
</tr>
<tr>
<td>11</td>
<td>Recovered 2nd time, 25</td>
<td>10</td>
<td>200</td>
<td>5</td>
<td>0.36</td>
<td>Recovered solvent, 20 mL</td>
</tr>
</tbody>
</table>
2.3.2.1.2 Effect of solvent volume and catalyst amount

In the solvothermal reactions, the operating pressure of the reaction played a vital role and has pronounced effect on the yield as well as the morphology of the obtained product. The reaction pressure can be altered by varying the reactor temperature or solvent (reactant) volume. The decrease in the quantity of tetrachloroethylene (10 mL) resulted in the higher yield (Table 2.3.3). This may be because of higher amount of solvents consumes the copper metal for formation of intermediate products which could not be completely reduced to carbon structures. It is observed that only 5 mL of tetrachloroethylene is consumed during the reaction. Hence, by using appropriate amount of solvent (10 mL), the reaction yield can be improved due the maximum utilization of copper metal for complete reduction. The increase in the amount of copper leads to higher yield and supports the above observations (Table 2.3.3). The increase in the amount of catalyst (Fig. 2.3.1d) and decrease in volume of solvent (Fig. 2.3.1e) leads to better yield but the formation of amorphous carbon as a byproduct also increases.

2.3.2.1.3 Recovery and reusability of carbon source

After the completion of reaction, the unreacted tetrachloroethylene could be recovered by filtration. It was observed that only 5 mL tetrachloroethylene out of 25 mL was consumed during the reaction. The recovered tetrachloroethylene was further used as carbon source, the obtained results showed that the formation and morphology of HSCNTs is not affected by reusing tetrachloroethylene and recovered solvent could be reused for the preparation next batch of HSCNTs. The yield was reduced to half when the recovered tetrachloroethylene used as carbon source.

2.3.2.1.4 Catalyst variation study

Various catalysts have been reported for the preparation of carbon nanostructures using dechlorination and solvothermal methods [36, 59]. Herewith we have studied the different metal powder such as nickel, iron, zinc, manganese and aluminum (5.0 g) as alternative reducing agents with tetrachloroethylene (25 mL) at 200 °C for 5 h, but reaction did not occurred with any one of the above catalyst. Only copper metal among the all metals used in the study, acts as reducing agent to produce the carbon material using tetrachloroethylene as carbon source.
2.3.2.2. Equilibrium gas adsorption study on HSCNTs

The HSCNTs obtained under optimized reaction condition (Table 2.3.3, entry 5) was further utilized for the adsorption study of gases such as CO\textsubscript{2}, CH\textsubscript{4}, CO and N\textsubscript{2}. Fig. 2.3.6a-c shows the adsorption isotherms of these pure gases at 288, 303 and 318 K respectively. The adsorption isotherms of all the gases under study followed the type-I isotherm showing the physisorption of adsorbate involving the intermolecular forces (Van der Waals forces). Among the studied gases, the maximum adsorption capacity for CO\textsubscript{2} of HSCNTs was 2.45, 2.01 and 1.53 mmol/g at 288, 303 and 318 K respectively. Fig. 2.3.6a-c clearly indicated higher adsorption value for CO over CH\textsubscript{4} in the lower (< 50 kPa) pressure range. The adsorption plots of CO and methane were crossing each other at > 50 kPa pressure, which resulted in to the tunable selectivity of CO over CH\textsubscript{4} in HSCNTs i.e. at lower pressure (< 50 kPa) the HSCNTs was selective towards CO whereas at higher pressure (> 50, < 113 kPa) the HSCNTs was selective towards CH\textsubscript{4}.
the reverse trend was observed, though there is no much difference in adsorption capacity for CO and CH\textsubscript{4} at 113 kPa. The similar trend is also observed in case of CO over CO\textsubscript{2} but at very low (< 2 kPa) pressure region (Fig. 2.3.6d) in which the adsorption of CO is higher as compare to the CO\textsubscript{2} adsorption before the crossing section. The crossing point of adsorption isotherms of CO and CO\textsubscript{2} within this range is shifted towards comparatively higher pressure with increasing adsorption temperature. Although, the CO\textsubscript{2} adsorption capacity of HSCNTs is comparable with activated carbon [60, 61], the adsorption of CO\textsubscript{2} per unit surface area is high in case of HSCNTs. The high adsorption capacity of HSCNTs may be due to the mesoporous structure as well as the surface functionality on the carbon nanotubes. Due to the use of CO in fine chemicals synthesis, the materials possessing selective and high adsorption capacity for CO have been attending great attention for separation and recovery of CO from gas mixtures. Various modifications in adsorbent have been reported for the enhancement in CO adsorption capacity. Ma et al. [62] reported the Cu decorated carbon as adsorbent for the CO adsorption, the CO adsorption capacity of adsorbent could be greatly increased by doping with the Cu salts. The pristine HSCNTs showed the high CO adsorption capacity due to the presence of Cu salt in the product (detected by EDX analysis). HSCNTs showed the comparatively high uptake capacity for CO which was 0.80, 0.74 and 0.51 mmol/g at 288, 303 and 318 K respectively.

The adsorption of different gas molecules on HSCNTs followed the equilibrium adsorption mechanism based upon the fundamental molecular properties of adsorbate such as quadrupole moment, dipole moment, polarizability and kinetic diameter which plays vital role in adsorbate-adsorbent interaction. Table 2.3.4 listed the molecular properties of adsorbate gases [63]. The kinetic diameter of the adsorbate molecules are in the range of 3.5-4.0 Å. The quadrupole moment and polarizability of adsorbate gases has the major impact on the adsorption phenomenon and are in the order CO\textsubscript{2} > CO > N\textsubscript{2} and CO\textsubscript{2} > CH\textsubscript{4} > CO > N\textsubscript{2} respectively. The maximum adsorption capacity obtained for CO\textsubscript{2} among the other gases on HSCNTs is due its higher quadrupole moment as well as high polarizability. The high polarizability of CH\textsubscript{4} than N\textsubscript{2} resulted in higher adsorption of CH\textsubscript{4} on HSCNTs compared to N\textsubscript{2} instead of its non-polar nature. The adsorption capacity of HSCNTs at 113 kPa followed the order CO\textsubscript{2} > CH\textsubscript{4} > CO > N\textsubscript{2} in accordance with the
polarizability of these gases and also observed by Phani et al. [63] in the case of MIL-53(Al) as adsorbent.

**Table 2.3.4 Properties of adsorbate gases**

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Mol. wt.</th>
<th>Kinetic diameter (Å)</th>
<th>Polarizability ($10^{-25}$ cm$^3$)</th>
<th>Dipole moment ($10^{18}$ esu.cm)</th>
<th>Quadrupole moment ($10^{-26}$ esu.cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>44</td>
<td>3.30</td>
<td>26.5</td>
<td>0.00</td>
<td>4.30</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>16</td>
<td>3.80</td>
<td>26.0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>3.76</td>
<td>19.5</td>
<td>0.112</td>
<td>2.50</td>
</tr>
<tr>
<td>N$_2$</td>
<td>28</td>
<td>3.64</td>
<td>17.6</td>
<td>0.00</td>
<td>1.52</td>
</tr>
</tbody>
</table>

The high uptake capacity with good selectivity is the main characteristic for the ideal adsorbent. Fig. 2.3.7a-c showed the adsorption capacity selectivity of various gases in HSCNTs at 288, 303 and 318 K respectively. The selectivity of carbon dioxide over nitrogen in HSCNTs was 6.1, 8.8 and 9.1 at 288, 303 and 318 K (113 kPa) respectively. HSCNTs showed good selectivity for carbon dioxide over nitrogen and the selectivity increased with decreasing the partial pressure (Fig. 2.3.7a-c). This selectivity trend is observed for all the gases except in case of selectivity of carbon dioxide over carbon monoxide. Slight increase in selectivity was observed at 40 kPa due to the high adsorption of CO than CO$_2$ at lower pressure. The obtained isotherm data were fitted into the Virial equation to obtain the Henry’s constant for adsorption of gases. Table 5 shows the Heat of adsorption, Henry’s constant and Virial coefficient for adsorption of different gases at various temperatures. Henry's constant is mainly depends upon the adsorption at lower pressure regions. The high adsorption of CO was observed in the lower pressure region and resulted in to the high value of Henry's constant for CO adsorption in horn shaped carbon nanotubes. The high uptake of CO at lower pressure range also resulted in to the compatible heat of adsorption of CO and CO$_2$ in horn shaped carbon nanotubes even though the total adsorption capacities of HSCNTs for CO and CO$_2$ have large difference.
**Fig. 2.3.7** Selectivity of different gases in HSCNTs; capacity selectivity at (a) 288 K, (b) 303 K, (c) 318 K and (d) equilibrium selectivity

**Table 2.3.5** Heat of adsorption, Henry’s constant and Virial coefficient at 288 K, 303 K and 318 K for CO₂, CH₄, CO and N₂ adsorption on HSCNTs

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Heat of adsorption (KJmol⁻¹)</th>
<th>Henry’s constant (10⁻³ mmol⁻¹ kPa⁻¹)</th>
<th>Virial coefficient A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>288 K</td>
<td>303 K</td>
</tr>
<tr>
<td>CO₂</td>
<td>29</td>
<td>165.5</td>
<td>78.9</td>
</tr>
<tr>
<td>CH₄</td>
<td>17</td>
<td>12.9</td>
<td>9.1</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>145.3</td>
<td>76.6</td>
</tr>
<tr>
<td>N₂</td>
<td>24</td>
<td>2.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The applicability of adsorbent material in gas separation techniques like pressure swing adsorption depend upon the equilibrium selectivity (determined using Henry’s constant) of adsorbent material for particular gas system. Fig. 2.3.7d showed the high equilibrium selectivity of HSCNTs for CO₂ and CO over nitrogen along with the moderate equilibrium selectivity in other cases such as CO₂/CH₄, CO/CH₄
and CH₄/N₂ at different temperatures studied; providing the use of HSCNTs as adsorbent material for separation of CO₂ and CO over nitrogen from flue and syngas/tail gases.

2.3.3 Conclusion

Horn shaped carbon nanotubes have been successfully synthesized by a dechlorination pathway at mild reaction conditions using tetrachloroethylene as carbon source with metallic copper as reducing agent. The reaction condition has been optimized by studying the effect of various reaction parameters on the yield as well as on the product morphology. The produced horn shaped carbon nanotubes showed rich surface functionality. The adsorption study on horn shaped carbon nanotubes showed high uptake capacity as well as high equilibrium selectivity of CO₂ and CO over N₂, and can be used as adsorbent material for the separation and recovery of gases.
2.4 Solid-state dechlorination pathway for the synthesis of few layered functionalized carbon nanosheets and their greenhouse gas adsorptivity over CO and N₂

2.4.1 Experimental

2.4.1.1 Synthesis of FCNS

Synthesis of FCNS was carried by heating the SS autoclave (50 ml capacity) containing hexachloroethane (6.2 g) and copper powder (5 g), at 300 °C for 5 h. After cooling the autoclave to room temperature, the obtained black color product was treated with 500 ml of 1:1 HNO₃ aqueous solution for 24 h under continuous stirring. The product was recovered by filtration, washed with deionized water till free from chloride ions and finally dried at 80 °C for 24 h. All required chemicals were procured from s. d. Fine Chem. Ltd. India and used as received.

2.4.1.2 Characterization of FCNS

The characterizations of obtained products were performed as described earlier in section 2.2.1.2.

2.4.1.3 Equilibrium gas adsorption study

The equilibrium gas adsorption study on FCNS was carried out as described earlier in section 2.3.1.3.

2.4.2 Results and discussion

2.4.2.1 FCNS synthesis

Fig. 2.4.1 SEM photograph of agglomerated FCNS
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The structural arrangement or morphology of the obtained carbon product investigated under SEM depicts an agglomerated form of FCNS. Fig. 2.4.1 indicated the particle nature of carbon nanosheets which provides the additional porosity to it. TEM analysis (Fig. 2.4.2a) also reflects the sheets like arrangement of the synthesized carbon product with randomly arranged wrinkled structure. The dark edges appeared in the TEM image (Fig. 2.4.2a) are the folded region of the FCNS with varying edge thickness of 6-12 nm. This type of wrinkled arrangement of FCNS was also observed by Kuang et al. [37] using methane tetrachloride as carbon source. Fig. 2.4.2b represents the high resolution TEM analysis of individual FCNS showed the irregular arrangement of lattice structure. The interlayer distance measured by multiple layers using the HRTEM analysis was ~0.344 nm and also in accordance with the XRD analysis.

The scheme 2.4.1 represents the chemical changes involved in the synthesis pathway of FCNS from hexachloroethane using copper as reductant under the autogenic pressure. The yield obtained in the present transformation was 0.24 g [3.8% on weight basis (C₂Cl₆) and 22.5 % on carbon content basis]. Although the both of reactants were taken in the (1:3) stoichiometric amount by considering the 100% reduction of hexachloroethane into the carbon, but the reactivity of copper was limited due to the coating/coverage of formed carbon product on the surface of the copper. Hence the 100% reduction of hexachloroethane into the carbon product was not attained in the present pathway thereby parting the chloride functional groups into the carbon texture.

Fig. 2.4.2 (a) TEM image of agglomerated crumbled FCNS with varying thickness and (b) HR-TEM image of individual FCNS
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\[ \text{C}_2\text{Cl}_6 + 3 \text{Cu} \xrightarrow{300 \, ^\circ \text{C}} 2 \text{C} + 3 \text{CuCl}_2 \]

Scheme 2.4.1

Fig. 2.4.3 XRD pattern of FCNS (a) before and (b) after acid washed

The vapors of hexachloroethane reacted with copper at 300 °C to produce the FCNS and copper (II) chloride as byproduct. The formation of CuCl₂ was confirmed by the XRD pattern of the as-synthesized product (Fig. 2.4.3a) showing intense peak matching with JSPSD file, No. 018-0439 of copper chloride hydroxide. The diffraction peaks for the CuCl and unreacted copper has also been observed with a lower intensity. The XRD pattern (Fig. 2.4.3b) of acid treated product showed the less intense broad diffraction peak for FCNS. The amorphous nature and irregular arrangement of carbon layers in obtained FCNS resulted into the broadening of 002 peak at \( \theta \) of 20-30° in the XRD pattern (Fig. 2.4.3b). The disappearance of diffraction peak observed for 001 plane at \( \theta \) of 43.5 also reflects the disorder of the FCNS.

FT-Raman analysis provided the vital information on the structure of the prepared FCNS. The Raman spectra of the FCNS (Fig. 2.4.4a) depict three bands namely D-band, G-band and 2D-band. The D-band observed at 1359 cm⁻¹ associated with the defect or disorder in the FCNS structure. The comparable intensity of the D- and G-band showed the defects in the prepared FCNS. The G-band, representing the planner configuration of sp² bonded carbon structure, is normally observed at \( \sim 1582 \) cm⁻¹ in case of single layer graphene. In case of obtained FCNS, the position of the G-band was shifted towards the higher wave number (1599 cm⁻¹) due to the increase in the sheet thickness. The effect of irregular layer thickness with disordered arrangement and in-situ functionalization of nanosheets was also reflected in the
shifting and broadening of 2D-band (second order or overtone of D-band) and resulted into the mixing with D+G band (normally observed at 2910 cm\(^{-1}\)). The effect of layer thickness and functionalization on the 2D-band was also noticed by the Hong et al. [29] and Subrahmanyam et al. [64]. Ferrari and Robertson [65, 66] provided a better description for the disorder induced in the carbon network and derived a new relation for the topological disordered in the graphite/graphene due to the introduction of 20% \(sp^3\) characters. The in-plane crystalline size calculated using Ferrari and Robertson formula, \([\frac{I_D}{I_G}] = C \cdot L^2\) was 12.4 nm (C \(\approx 0.0055\) for 514 nm).

![Figure 2.4.4: FT-Raman and FT-IR spectrum of FCNS prepared using hexachloroethane](image)

**Fig. 2.4.4** (a) FT-Raman and (b) FT-IR spectrum of FCNS prepared using hexachloroethane

The FT-IR analysis of carbon product before and after nitric acid treatment (Fig. 2.4.4) clearly showed the introduction of the oxygen containing functional groups such as \(-\text{COOH}, -\text{OH}, -\text{C=O}, -\text{O=C} \text{ into the FCNS during the acid treatment. The band at 3400 cm}^{-1}\) was associated with stretching of hydrogen bonded \(-\text{OH},\) whereas \(\text{C=O}\) group was characterized by the stretching mode at 1708 cm\(^{-1}\). The \(sp^2\) hybridized \(\text{C=C}\) bond was clearly indicated by the strong absorption band at 1600 cm\(^{-1}\). The \(\text{C–O}\) and \(\text{C–H}\) stretching vibration was also observed at 1250 and 2920 cm\(^{-1}\) respectively. The oxygen content of FCNS (35.3 wt\%) analyzed by EDX analysis also support the above observations. The carbon, chlorine and copper content of the FCNS (by EDX analysis) were 62.8, 1.4 and 0.5 wt\% respectively. The elemental analysis of FCNS [60.2\% (C) and 1.1\% (H)] was also in good agreement with the above results.
The thermal stability of the prepared FCNS was evaluated with the TGA analysis under nitrogen flow. Fig. 2.4.5 showed the percentage decrease in weight of the FCNS with respect to temperature. The major weight loss (16.5%) in the FCNS was observed in the range of the 400 to 600 °C due to the degradation of the carbonyl containing functional groups such as –COOH, C=O, lactone, etc., whereas the second major weight loss (130-320 °C, 8.8%) was due to the decomposition of hydroxyl groups and the chemisorbed water molecules. The moisture or physisorbed water (4.1%) was removed at < 130 °C. The total weight loss of the obtained FCNS was ~29.4% up to 700 °C in the nitrogen atmosphere. The surface functionality (mainly oxygen containing functional group) present on the FCNS makes it thermally less stable compared to pure carbon materials.

The surface area or the texture properties of the carbon materials plays an important role in their prospective applications such as adsorbent material, catalyst support and sensors etc. Graphene possesses the very high theoretical surface area of 2650 m²/g, however, this is yet to be achieved due to agglomerated nature of the synthesized graphene sheets. The surface area of the FCNS prepared using present protocol (Table 2.4.1) was determined with nitrogen sorption at 77 K. The nitrogen sorption on FCNS exhibits (Fig. 2.4.6) the Type IIb physisorption isotherm classified by IUPAC, characteristics of the mesoporous materials. The hysteresis loop of Type-H4 exhibits the filling and emptying of the mesopores by capillary condensation. The pore size distribution of the FCNS determined using BJH method with
desorption data showed the FCNS contains the maximum pores in the range of 3-4 nm (mesopores) and majorly contributed to the total pore volume whereas the adsorption average pore width is 4.2 nm (determined using 4V/A by BET).

Fig. 2.4.6 Isotherm showing the sorption of nitrogen molecules on FCNS at 77 K, inset figure showing the pore size distribution of FCNS determined by applying BJH method to desorption data

Table 2.4.1 Specific surface areas, specific pore volumes and average pore size of FCNS

<table>
<thead>
<tr>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_BET⁴</td>
<td>S_Lang⁵</td>
<td>S_micro⁶</td>
</tr>
<tr>
<td>836.3</td>
<td>1079.3</td>
<td>312.8</td>
</tr>
</tbody>
</table>

⁴Brunauer-Emmer-Teller (BET) surface area, ⁵Langmuir Surface Area, ⁶Micropore surface area, calculated using t-plot method, ⁷External surface area, calculated using t-plot method, ⁸Single point adsorption total pore volume, obtained at P/P₀ = 0.9732, ⁹t-Plot micro pore volume, ¹⁰Adsorption average pore diameter, obtained from 4V/A by BET, ¹¹BJH desorption average pore diameter
Chapter 2 Synthesis of carbon nanomaterials using chloro-hydrocarbons as carbon source

2.4.2.2 Greenhouse gas adsorptivity of FCNS over CO and N₂

2.4.2.2.1 Adsorption equilibrium

The obtained FCNS was utilized as the adsorbent for the adsorption of CO₂, CH₄, CO and N₂. The adsorption isotherms of CO₂, CH₄, CO and N₂ on FCNS at 288, 303, 318 K and gas pressure up to 113 kPa are given in Fig. 2.4.7. All adsorption isotherms were found to be similar with the Type-I classified by IUPAC showing the stronger adsorbate-adsorbent interaction than adsorbate-adsorbate interaction in the bulk state. FCNS showed the highest adsorption capacity for carbon dioxide (2.95 mmol/g at 288 K; 2.24 mmol/g at 303 K and 1.64 mmol/g at 318 K) followed by carbon monoxide (1.34 mmol/g at 288 K; 1.06 mmol/g at 303 K and 0.73 mmol/g at 318 K), methane (1.12 mmol/g at 288 K; 0.81 mmol/g at 303 K and 0.55 mmol/g at 318 K) and nitrogen (0.39 mmol/g at 288 K; 0.27 cm³/g at 303 K and 0.16 mmol/g at 318 K) at all studied temperatures. The carbon monoxide showed the higher affinity towards the FCNS at lower pressure as compared to the other gases although the carbon dioxide possesses the high adsorption capacity at 113 kPa. In the case of carbon adsorbents, non-specific interactions such as dispersion and close-range repulsion energy plays an important role during adsorption due to the absence/less amount of charges on the surface [67]. Therefore the polarizability of gases governs their adsorption on carbon materials. Carbon dioxide, possessing the higher polarizability showed the higher adsorption than the other studied gases at final pressure. The high adsorption affinity between the FCNS and carbon monoxide at lower pressure can be attributed to the copper adventitiously present in minute quantities in FCNS. The Cu salt incorporated activated carbon has been used commercially for the carbon monoxide separation [67]. The enhancement in the carbon monoxide adsorption in FCNS may be due to the formation of π complexation between copper and carbon monoxide.

The FT-IR spectrum of the FCNS (Fig. 2.4.8) in the carbon monoxide atmosphere clearly showed the two additional adsorption bands at 2117 and 2174 cm⁻¹ attributed for Cu-CO interaction [68, 69]. The presence of the element with high polarizability also improves the adsorption affinity for adsorbate due to the enhancement in the dispersion potential of adsorbent [67]. Chlorine (2.18) possesses the high polarizability than the carbon (1.76), hence the presence of chlorine atom in
the texture of the FCNS also have advantageous for adsorption. The low adsorption capacity and linear shape of the nitrogen isotherm showed the weaker interaction of nitrogen with FCNS due to the lower polarizability.

Fig. 2.4.7 Carbon dioxide, carbon monoxide, methane and nitrogen gas adsorption isotherm on CNS at (a) 288 (b) 303 and (c) 318 K

Fig. 2.4.8 FT-IR spectra of FCNS before and after carbon monoxide adsorption
From the different proposed models for evaluation of the experimental gas adsorption data, Langmuir and Freundlich models were used to correlate the experimental adsorption data using non-linear regression method [70, 71]. The data was fitted with help of Origin Pro 9.0 software.

The Langmuir isotherm [72] is written as:

\[ q = \frac{q_m B P}{1 + B P} \]  

Eq. 2.4.1

The Freundlich Isotherm [73] is written as:

\[ q = k P^{1/n} \]  

Eq. 2.4.2

where \( q \) is the amount of gas adsorbed (mmol/g), \( P \) is the equilibrium pressure (kPa), \( q_m \) is the monolayer adsorption capacity (mmol/g), \( B \) is the Langmuir constant (kPa\(^{-1}\)), \( k \) (mmol/g) and \( n \) are the Freundlich parameters related with the adsorption capacity and adsorption intensity respectively.

The regression coefficient (\( R^2 \)) and average relative error (ARE) methods were used to estimate the degree of fitness of each isotherm.

Calculation of ARE was carried by following formula and given in Table 2.4.2.

\[ \%\text{ARE} = \left( \frac{|q - q_{\text{cal}}|}{q} \right) \times 100/N \]  

Eq. 2.4.3

where \( q \) is the experimental adsorption amount, \( q_{\text{cal}} \) is calculated adsorption amount using models and \( N \) is the number of adsorption points.

Fig. 2.4.9 shows the fitting of Langmuir and Freundlich models to experimental adsorption isotherms for nitrogen, methane, carbon monoxide and carbon dioxide on FCNS at 288, 303 and 318 K. In case of nitrogen and methane, the both Langmuir and Freundlich models (Fig. 2.4.9a and b) were well fitted with the experimental data having the regression coefficient of > 0.99, due to linear nature of the isotherm and the lack of saturation in the adsorption capacity at studied pressure. The same observation was also noted by Khalili et al. [70] for nitrogen and carbon dioxide adsorption on multi-walled carbon nanotubes. The Freundlich adsorption model best explained the adsorption of carbon monoxide on FCNS (Fig. 2.4.9c, Table 2.4.2). The best fitting of Freundlich model for carbon monoxide adsorption also supports the multilayer adsorption of carbon monoxide on FCNS involving \( \pi \) complexation. Although the carbon dioxide adsorption on FCNS was more suitable
with Freundlich models (Fig. 2.4.9d), the regression coefficient values obtained with Langmuir model were also found satisfactory (> 0.99, Table 2.4.2). In case of carbon dioxide, the lower adsorption temperature favors the adsorbate-adsorbate interaction and formation of multilayer resulted into the best fitting with Freundlich model. The % ARE (Table 2.4.2) calculated from the experimental and simulated gas adsorption data also supported the above findings.
Table 2.4.2 Langmuir and Freundlich isotherm constant for adsorption of nitrogen, methane, carbon monoxide and carbon dioxide on FCNS

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Temperature (K)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$q_m$</td>
<td>$B$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>288</td>
<td>2.05</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>2.18</td>
<td>0.0012</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1.25</td>
<td>0.0013</td>
</tr>
<tr>
<td>Methane</td>
<td>288</td>
<td>2.75</td>
<td>0.0059</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>2.59</td>
<td>0.0038</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1.69</td>
<td>0.0042</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>288</td>
<td>1.50</td>
<td>0.0348</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.26</td>
<td>0.0281</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.80</td>
<td>0.0373</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>288</td>
<td>4.31</td>
<td>0.0162</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>3.38</td>
<td>0.0150</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>3.09</td>
<td>0.0095</td>
</tr>
</tbody>
</table>
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Synthesis of carbon nanomaterials using chloro-hydrocarbons as carbon source

Sandesh Y. Sawant  
Ph.D. Thesis

Fig. 2.4.9 The experimental and stimulated (Langmuir and Freundlich) adsorption isotherms of (a) nitrogen, (b) methane, (c) carbon monoxide and (d) carbon dioxide on FCNS at different temperatures

2.4.2.2.2 Adsorption selectivity

The high adsorption capacity and selectivity is the basic criteria for the adsorbent utilized in the gas separation applications. The adsorbent material possessing high adsorption capacity but low selectivity is not useful for the gas separation. Fuel gas exhausting from the power stations mainly contains carbon dioxide (10-14%) along with nitrogen and carbon monoxide. Hence for the separation of the carbon dioxide and carbon monoxide requires the adsorbent material with high selectivity for these gases over nitrogen.

Fig. 2.4.10 showed the plot of capacity selectivity and equilibrium selectivity of FCNS for carbon dioxide, carbon monoxide, methane and nitrogen over each other at different temperature and equilibrium pressure. The FCNS showed the higher capacity selectivity for carbon dioxide over nitrogen (8.4) followed by
methane (2.8) and carbon monoxide (2.1) at 303 K. The decrease in the capacity selectivity was observed with increase in the pressure. The decrease in the capacity selectivity over pressure was attributed to the decrease in the adsorption capacity with pressure of other adsorbate in comparison with linear adsorption of nitrogen on FCNS. The exception was observed with above findings in case of selectivity of carbon dioxide over carbon monoxide due to the initially high adsorption affinity of carbon monoxide to FCNS.

The capacity selectivity trend for the gases studied was CO\textsubscript{2}/N\textsubscript{2} > CO/N\textsubscript{2} > CH\textsubscript{4}/N\textsubscript{2} > CO\textsubscript{2}/CH\textsubscript{4} > CO\textsubscript{2}/CO > CO/CH\textsubscript{4} at all studied temperatures because of the high adsorption capacity of FCNS for CO\textsubscript{2} and CO. Both the pore size distribution and surface functionality played an important role in the adsorption capacity by effecting adsorbate-adsorbent interaction. The micropore volume with uniform pore size distribution is more favorable for the gas adsorption on carbon material \cite{74, 75}. Such type of uniform microporosity can be achieved in the carbon material.

\begin{figure}[h]  
\centering  
\includegraphics[width=\textwidth]{selectivity.png}  
\caption{Capacity selectivity of FCNS at (a) 288, (b) 303, (c) 318 K and (d) equilibrium selectivity at different temperatures}  
\end{figure}
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synthesized using zeolite as template. Boisgontier et al. [76] synthesized the zeolite templated carbon replicas having high micropore volume with uniform pore size distribution. The prepared carbon replicas showed the maximum equilibrium selectivity of 2.9 and 8.4 for carbon dioxide over methane and nitrogen respectively. Here the adsorbate properties and pore structure of carbon replicas were responsible for the adsorption and separation efficiency. The hydrophobic nature (i.e. less surface oxygen functionality) of the carbon material is favorable for methane adsorption [77, 78]. Contreras et al. [75] also supported the above findings and observed the significant enhancement in the methane adsorption capacity of the commercial activated carbon thorough the elimination of oxygen functionality by heat treatment. The simulation and experimental studies showed that the oxygen functionality such as hydroxyl, carbonyl, carboxylic, etc. significantly influenced the electrostatic adsorbate-adsorbent interactions and favors the carbon dioxide adsorption on carbon materials [79, 80]. The obtained FCNS possesses the larger average pore diameters (3-4 nm) in comparison with the kinetic diameters of the adsorbate gas molecules (< 3.9 Å) and hence have negligible effect on the selectivity. The high oxygen surface functionality of FCNS supports the high adsorption as well as selectivity for the carbon dioxide as compared to the other adsorbents due to the electrostatic interaction of carbon dioxide with oxygen-containing functional groups. Furmaniak et al. [81] observed the effect of carbon pore size and oxygen functionality on the carbon dioxide and methane selectivity. The introduction of the oxygen functional groups enhances the carbon dioxide equilibrium selectivity over methane (~ 2-3 times) than the parent carbon material, and same phenomena is also expected for the adsorbate possessing the weaker electrostatic and dispersion interactions [81].

The equilibrium selectivity of the materials decides the theoretical separation efficiency of the adsorbent at particular temperature. The zeolites are widely used as commercial adsorbent for carbon dioxide separation from flue gas due to their low cost and high equilibrium selectivity for carbon dioxide over nitrogen. The FCNS obtained in the present study showed the high equilibrium selectivity of 197, 197 and 193 for carbon monoxide over nitrogen at 288, 303 and 318 K respectively (Fig. 2.4.10d). Although, the FCNS possesses the high CO₂ adsorption capacity than CO, the equilibrium selectivity of carbon dioxide was less (27 at 288 K, 26 at 303 K and
18 at 318 K) than that of CO over nitrogen. The high loading of carbon monoxide on FCNS at lower pressure due to the Cu-CO interaction attributed for the high value of Henry's constant (Table 2.4.4) than that of carbon dioxide and resulted into the high equilibrium selectivity. Besides, FCNS also showed good equilibrium selectivity for carbon monoxide over carbon dioxide and methane at all studied temperature (Fig. 2.4.10). The equilibrium selectivity of FCNS for carbon dioxide over methane (5.7) and methane over nitrogen (4.5) at 303 K was also promising. Table 2.4.3 shows the comparison of maximum adsorption capacity, capacity and equilibrium selectivity of different adsorbent materials for CO₂, CH₄ and N₂ adsorption under different conditions. Hence the FCNS can be a potential adsorbent material for carbon dioxide/carbon monoxide separation due to its high equilibrium selectivity and adsorption capacity for CO₂ and CO.

The positive sign of heat of adsorption indicated the adsorption of studied gases on FCNS was exothermic process. The carbon monoxide adsorption on FCNS associated with the higher heat of adsorption followed by carbon dioxide, methane and nitrogen showing the greater interaction of the carbon monoxide with FCNS.
Table 2.4.3 Comparison of maximum adsorption capacity, capacity and equilibrium selectivity of different adsorbent materials for CO₂, CH₄ and N₂ adsorption

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Maximum adsorption capacity (cc/g)</th>
<th>Condition</th>
<th>Capacity Selectivity</th>
<th>Equilibrium selectivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>CH₄</td>
<td>N₂</td>
<td></td>
<td>CO₂/N₂</td>
</tr>
<tr>
<td>Silicalite</td>
<td>~36.0</td>
<td>~13.0</td>
<td>~4.5</td>
<td>294 K, 101 kPa</td>
<td>8.0</td>
</tr>
<tr>
<td>High silica zeolite</td>
<td>46.3</td>
<td>15.5</td>
<td>4.6</td>
<td>298 K, 101 kPa</td>
<td>10.1</td>
</tr>
<tr>
<td>Zeolite-5A</td>
<td>105.9</td>
<td>18.9</td>
<td>12.6</td>
<td>298 K, 107 kPa</td>
<td>8.4</td>
</tr>
<tr>
<td>MOF-508b</td>
<td>132.4</td>
<td>44.8</td>
<td>44.0</td>
<td>303k, 450 kPa</td>
<td>3.0</td>
</tr>
<tr>
<td>CuBTC, sample-b</td>
<td>104.2</td>
<td>21.3</td>
<td>7.8</td>
<td>295 K, 100 kPa</td>
<td>13.4</td>
</tr>
<tr>
<td>MOF-5</td>
<td>244.3</td>
<td>240.1</td>
<td>---</td>
<td>298 K, 1.4 MPa</td>
<td>---</td>
</tr>
<tr>
<td>MOF-177</td>
<td>202.1</td>
<td>308.4</td>
<td>---</td>
<td>298 K, 1.4 MPa</td>
<td>---</td>
</tr>
<tr>
<td>Benzene deposited CMS</td>
<td>22.0</td>
<td>2.2</td>
<td>2.4</td>
<td>298 K, 48 kPa</td>
<td>9.2</td>
</tr>
<tr>
<td>PEI-oil palm shell (CMB)</td>
<td>51.1</td>
<td>15.7</td>
<td>6.6</td>
<td>298 K, 107 kPa</td>
<td>7.8</td>
</tr>
<tr>
<td>HSCNNTs</td>
<td>45.1</td>
<td>17.0</td>
<td>5.1</td>
<td>303 K, 113 kPa</td>
<td>8.8</td>
</tr>
<tr>
<td>FCNS</td>
<td>2.24</td>
<td>0.81</td>
<td>0.27</td>
<td>303 K, 113 kPa</td>
<td>8.4</td>
</tr>
</tbody>
</table>
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Table 2.4.4 Heat of adsorption, Henry’s constant and Virial coefficient at 288, 303 and 318 K for CO₂, CH₄, CO and N₂ adsorption on CNS

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Heat of adsorption (kJmol⁻¹)</th>
<th>Henry’s constant (10⁻³mmolg⁻¹kPa⁻¹)</th>
<th>Virial coefficient A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>288 K</td>
<td>303 K</td>
</tr>
<tr>
<td>CO₂</td>
<td>28.8</td>
<td>80.8</td>
<td>50.1</td>
</tr>
<tr>
<td>CO</td>
<td>39.2</td>
<td>591.0</td>
<td>385.6</td>
</tr>
<tr>
<td>CH₄</td>
<td>25.1</td>
<td>10.0</td>
<td>8.8</td>
</tr>
<tr>
<td>N₂</td>
<td>24.0</td>
<td>3.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

2.4.3 Conclusion

Few layered FCNS was successfully synthesized using hexachloroethane as carbon source and copper powder as reducing agent under autogenic pressurized condition. The obtained CNS showed the varying layer thickness of 6-12 nm (as characterized by TEM analysis) and possesses the surface and textural oxygen, and chlorine functionality. The equilibrium gas adsorption study of greenhouse gases (CO₂ and CH₄), toxic gas (CO) and light gas (N₂) showed that the FCNS possesses the high adsorption capacity for CO₂ over CO, CH₄ and N₂. The carbon monoxide showed greater binding tendency towards FCNS at lower pressure due to the copper adventitiously present in minute quantities in FCNS and resulted into highest equilibrium selectivity for CO over other gases at different temperatures. The π complexation of CO with copper on FCNS was also supported by the FT-IR analysis. The adsorption of N₂ and CH₄ on FCNS was fitted with the both Langmuir and Freundlich model whereas the CO adsorption exhibits better fit for Freundlich model. In the case of carbon dioxide, the lower adsorption temperature favors the adsorbate-adsorbate interaction and formation of multilayer resulted into the best fitting with Freundlich model.
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