CHAPTER 4

CONCLUSION

Worldwide extensive and intensive researches on the preparation, characterization and applications of carbon nanotubes have been performed for the past 15 years. The nano-size effects show unique size distribution and hollow geometry, which result in unique electrical, mechanical, physical and chemical properties and finds its use in advanced scanning probes, electron field emission sources, hydrogen storage materials and building blocks of molecular electronics. The extraordinary mechanical properties of CNTs and their reinforcements are potential for the production of ultra-strong nanocomposites. The fabricated epoxy nanocomposites are well-suited for aerospace applications. For commercial applications, the low cost production of well defined and organized arrays of CNTs, in sufficient quantities is of high importance. Generally, CNTs can be synthesized by various methods such as arc discharge, laser ablation and CVD. In the first two methods, solid-state carbons are used as a carbon source and needs high temperature to evaporate it. The CVD procedure has major advantages in comparison with the other known methods. They are (i) formation of CNTs at lower temperature, (ii) enhanced productivity, (iii) flexibility of the procedure which means that using the same equipment to produce either SWCNTs or MWCNTs by simply changing the reaction conditions and (iv) relative easy up-scaling.

The formation of CNTs mainly depends on various reaction parameters such as temperature, flow rate of carbon precursor and time. However, the nature of catalytic templates (support) such as porosity, surface area, dimension of the supported materials, thermal stability and amount of metal (mono and bi) over the support also play a vital role for the growth of CNTs. Compared to microporous zeolites as catalysts, the mesoporous MCM-41 materials discovered by the researchers of Mobil Oil Corporation and KIT-6 are considered as convenient candidates for the formation of CNTs. Mesoporous MCM-41 molecular sieves have unique physical properties such as extremely high surface area and large pore size, which allows for the fixation of large active complexes and enables reaction involving bulky molecules to take place at nearly nil diffusion constraint for the reactants to enter and the products to leave their mesopores. Hence it is proposed that MCM-41 materials with the incorporation of transition metals were considered as the best choice for the formation of uniform diameter distribution of SWCNTs and MWCNTs. In general, transition metals such as Fe, Co and Ni were considered as good candidates for the formation of CNTs in high yield. Hence, the transition metals such as Fe, Zn, Cr and Zn-Fe were incorporated in the framework of MCM-41 by hydrothermal synthesis. Some of the transition metals such as Fe, Co, Mn, Ni, Ti, Ru and Pd were loaded over Cr-MCM-41 and Antimony (Sb) was supported over Si-MCM-41 by wet impregnation method. Among the mesoporous materials, KIT-6 have several advantages such as high thermal stability due to construction of walls, large tunable pores and significantly KIT-6 exhibits a three-dimensional cubic Ia3d symmetric structure with interpenetrating bicontinuous network of channels. This provides highly opened spaces for direct access to guest species without pore blockage due to their unique 3D channel networks. The metal incorporated and impregnated mesoporous 3D cubic KIT-6 molecular sieves were suitable candidate for the production of well graphitized MWCNTs. In this study, different synthesis parameters such as reaction temperature, flow rate of acetylene, mono and bimetal effect, amount of metal over the mesoporous materials and reaction time were investigated for the better growth of CNTs.

4.1 PERSPECTIVES OF THE PRESENT INVESTIGATION

The mono and bimetal-containing MCM-41, KIT-6 and MgO were used as the catalytic templates for the synthesis of CNTs by CVD method. Physico-chemical characterizations confirmed the synthesized catalytic templates were well ordered mesopores with uniform pore diameters and also formed CNTs were found to be well graphitized.

The mesoporous Fe-MCM-41 (Si/Fe ratios of 50, 75, 100 and 125), Zn-MCM-41 (Si/Zn ratios of 50, 75, 100 and 125) and Zn-Fe-MCM-41 (100) (Fe:Zn ratios of 1:4, 1:3, 1:2, 1:1, 2:1, 3:1 and 4:1) were synthesized by hydrothermal method. All these mesoporous materials were found to possess pore diameter around 2.5 nm. The specific surface area of samples determined by the BET surface area lies in the range of 923–978 m^2/g for Zn-MCM-41 (100), Zn-Fe-MCM-41 (100) and Fe-MCM-41 (100). In the catalytic synthesis of CNTs over mesoporous Zn-Fe-MCM-41 molecular sieves, Fe:Zn (3:1) produced SWCNTs in large quantity and are of high quality when compared with that obtained for other ratios. The synthesis yield was easily estimated after removing the support by a simple acidic treatment to obtain SWCNTs of high purity. The CVD method of synthesis could replace the other two methods of CNTs production, because of low temperature conditions (800 ºC), low cost of production, growth location, as well as controls the NT's diameter by adjusting the size of metal particles and its industrial application potential. The formation of SWCNTs with a diameter in the range of 1.2–2.5 nm was observed from Raman spectrum. The good thermal stability and high productivity observed in this study suggested that the Zn-Fe-MCM-41 mesoporous molecular sieves could be a kind of promising supports for the synthesis of SWCNTs.

Structural stability, thermal stability, porosity and morphology of Cr-MCM-41 and M/Cr-MCM-41 (where M = Fe, Co, Mn, Ni, Ti, Ru and Pd) materials were confirmed by various physico-chemical techniques. MWCNTs were catalytically synthesized by the decomposition of acetylene using Cr-MCM-41 and M/Cr-MCM-41 catalyst at 800 °C. The combinations of Fe or Pd with Cr were found to be more active to produce MWCNTs with high purity and great magnitude when compared with that produced by other mono and bimetallic catalysts. The absence of the catalytic template in MWCNTs was confirmed by SEM and TEM images of purified MWCNTs. The formation of MWCNTs with uniform inner diameter in the range of 4–5 nm and outer diameter in the range of 12−13 nm was observed over Fe/Cr-MCM-41. The Pd/Cr-MCM-41 catalytic template produced MWCNTs in the diameter range of 6–7 nm and 16−17 nm inner and outer, respectively. The high quality of MWCNTs arrays without major contamination is observed from HR-TEM. High qualities of MWCNTs without SWCNTs and other carbonaceous impurities were confirmed by Raman studies. The good thermal stability and high productivity revealed from the studies suggested that the Fe/Cr-MCM-41 and Pd/Cr-MCM-41 mesoporous molecular sieves could be suitable supports for catalytically synthesizing MWCNTs by CVD method.

Antimony loaded over Si-MCM-41 with different wt. % was prepared by wet impregnation method. The bulk metal clusters were formed over Si-MCM-41 while increasing the Sb concentration over Si-MCM-41 but the hexagonality was not much affected. The MWCNTs were catalytically synthesized by the decomposition of acetylene over Sb/MCM-41 with different wt. % at various temperatures (700, 800, 900 and 1000 °C) by CVD method. The 2 wt. % of Sb/MCM-41 was found to produce MWCNTs with high quality and large quantity when compared with that obtained by other wt. % of Sb/MCM-41 at 800 °C. The formation of MWCNTs with an inner diameter in the range of 4–6 nm was observed from HR-TEM. In general, CNTs possess electrical properties, in addition to that Sb/MCM-41 produced MWCNTs act as a semiconducting materials due to trace amount of Sb metal particle present in the MWCNTs which may provide space for electrical and electronic applications. Also, Sb/MCM-41 produced MWCNTs having several internal compartments may induce the storage capacity in respective fields.

Tailored mesoporous 3D cubic KIT-6 catalytic templates were found to be highly ordered as confirmed by various physico-chemical techniques. The large pore size and pore volume were calculated from nitrogen sorption isotherm studies. The synthesized mesoporous materials were used as the catalytic template for the production of MWCNTs. The MWCNTs were catalytically synthesized by decomposition of acetylene over 0.5 wt. % of Zn-Fe-KIT-6 (75) catalyst at 800 °C which showed better formation when compared with that obtained by other wt. % and ratios of Fe-KIT-6 (50 and 100). KIT-6 provides highly opened spaces for direct access to guest species without pore blockage due to their unique 3D channel networks. Zn/Fe-KIT-6 was found to be better template for the growth of MWCNTs than Zn/Fe-MCM-41. The synthesized MWCNTs were found to have inner and outer diameter ranging from 8–9 nm and 30–32 nm respectively, which were observed from HR-TEM. The well graphitization was confirmed by Raman spectrum and XRD pattern. Zn/Fe-KIT-6 produced MWCNTs may show a way to many future applications, especially thermo-mechanical applications due to narrow inner diameter and more number of graphene layers present in the NTs. The Zn/Fe-KIT-6 produced MWCNTs were stronger than that obtained from MCM-41 and metal oxide. Catalytic particles were completely absent in MWCNTs after purification which was revealed by XRD pattern, SEM and TEM images. Further these purified MWCNTs were functionalized to form hydroxide groups (around 3432 cm^{-1}) and carbonyl groups (around 1660 cm^{-1}) over them to enhance the thermo-mechanical properties of nanocomposites. The carboxylic groups were functionalized over the MWCNTs without major structural defects.

The impregnated Zn-Fe/MgO and C_2H_2 were used as catalytic template and carbon precursor respectively for the production of MWCNTs by CVD method at different temperatures. Among various weight percentages of 3:1 ratio of Fe and Zn loaded MgO, 2 wt. % loading was found to be better for the formation of MWCNTs at 800 °C. These MWCNTs produced over metal oxides were broadly distributed in the diameter range. The inner and outer diameter of the MWCNTs measured from HR-TEM observations were in the range of 5–8 nm and 18–22 nm, respectively. The mesoporous metal containing KIT-6 produced MWCNTs possess high thermo-mechanical stability due to their wall thickness. The MWCNTs were functionalized and then the functional groups were identified by FT-IR spectroscopy. Both Zn/Fe-KIT-6 and Zn-Fe/MgO produced MWCNTs and f-MWCNTs were used as filler materials for the fabrication of epoxy nanocomposites.

Major disadvantages of neat epoxy resins such as low peel, low impact and low tensile strength at elevated temperatures, low chemical resistance limits their applications. In the present study, it was aimed at improving the thermo-mechanical properties of the neat epoxy resin by the addition of fillers such as MWCNTs and f-MWCNTs. The neat epoxy matrix and various wt. % (0.5, 1.0 and 1.5) of MWCNTs or f-MWCNTs containing epoxy nanocomposites were fabricated by casting method. The thermo-mechanical tests were conducted on neat epoxy and MWCNTs/Epoxy and f-MWCNTs/Epoxy nanocomposites. Based on the experimental results, the

1 wt. % of MWCNTs and/or f-MWCNTs loaded epoxy resin showed the highest improvement in tensile strength, flexural strength and hardness as compared with neat and other epoxy systems. The rate of burning decreased with respect to the wt. % of MWCNTs and f-MWCNTs observed from flame retardant test. Zn/Fe-KIT-6 produced MWCNTs were found to possess high thermo-mechanical properties when compared with Zn-Fe/MgO produced MWCNTs. It is evident that these MWCNTs and f-MWCNTs produced epoxy nanocomposites possess high thermo-mechanical properties.

The good thermal stability and high productivity observed in this study suggested that the transition metal (Zn-Fe, Pd/Cr, Fe/Cr and Sb) containing mesoporous molecular sieves would be a kind of promising supports for catalytically synthesizing CNTs. Thus, the experimental research work reveals that above said metal containing mesoporous materials can be convenient eco-friendly alternative to all other catalysts for the formation of SWCNTs and MWCNTs with high quality and large quantity. Especially, the metal containing mesoporous KIT-6 have high thermal stability and also were suitable candidate for large scale production of well graphitized MWCNTs. From the commercial and industrial point of view, the use of mesoporous materials and CVD method would be a promising technology to offer CNTs with high pure and highly selective SWCNTs and MWCNTs at a reasonable cost to the advanced modern world. Fabricated f-MWCNTs/Epoxy nanocomposites also exhibit good thermo-mechanical properties and opens new avenues for various industrial applications.

4.2 SCOPE OF FUTURE WORK

In future, synthesis and use of various novel nanomaterials as supports and efficient path for the production of CNTs are to be considered. The support materials need to be examined for the large scale production of SWCNTs and MWCNTs by CVD method. The effect of reaction parameters such as temperature, nature of carbon sources, time, flow rate, amount and properties of metals has to be optimized for the better formation of SWCNTs or MWCNTs. The synthesized SWCNTs or MWCNTs are necessary to be functionalized with various organic and bio-active compounds which can provide space for various applications. In particular, the bio-active compound functionalized CNTs finds its importance in various drug delivery systems depending on the nature of functional groups.