CHAPTER VIII
CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Silica-supported Co-Re catalysts were first used for SWNTs synthesis by CO disproportionation. The yield and selectivity towards SWNTs of Co-Re catalysts were found to be strongly depended on the reduction temperature, reaction temperature, and Co/Re ratio. The highest yield and selectivity were achieved with Co-Re(1:4)/SiO_2 when the catalyst was pretreated in H_2 at 800°C and the optimum reaction temperature was 850°C. The SWNTs obtained mainly consisted of 0.7-nm tubes which is the smallest diameter expected for capped SWNTs. It was found that at the optimum reduction temperature, all Co and Re oxides are completely reduced to metallic state at which the nanotubes are formed. However, the stabilization of Co species was found to occur in the Co-Re alloy phase, which is different from what was observed in the Co-Mo/SiO_2 catalyst. To predict the mechanism on the Co-Re/SiO_2 catalyst, interaction of Co and Re, which are responsible for the nanotubes growth, should be considered and investigated.

The synthesis of SWNTs by using catalytic decomposition of CO and CH_4 over different solid catalysts provides many interesting results. In case of silica-supported catalysts, both monometallic and bimetallic catalysts could be used to produce SWNTs under disproportionation of CO gas, but none of the catalysts in this series produced SWNTs when using CH_4 gas. The highest selectivity to SWNTs among the catalysts in this series was achieved with the use of CoMo(1:2)/SiO_2 and CO gas. In case of MgO-supported catalysts, only monometallic catalysts are active for SWNTs production, Co/MgO catalyst give high selectivity over other catalysts. In case of Al_2O_3-supported catalysts, only bimetalic catalysts are active for SWNTs production, CoMo(1:1)/Al_2O_3 with CO gas provide the best selectivity in this Al_2O_3-supported catalysts series. Finally, among all catalysts tested, the production of SWNTs by disproportionation reaction of CO over silica supported Co-Mo catalysts under studied operating conditions showed the best SWNTs quality.

In the preliminary study of froth flotation technique for SWNTs purification, silica gel removal and carbon black recovery by froth flotation were studied. It was found that, froth flotation can be used to separate hydrophobic particles from hydrophilic particles in aqueous solution. Since the point of zero charge (PZC) of the carbon black is close to that of the silica gel, a nonionic surfactant was used as the separating agent. To achieve a high recovery of carbon black, surfactant concentration should be optimized to generate voluminous, stable foams, but avoid silica gel entrainment to the top of the column. A surfactant concentration of 75% of the CMC, solid mixture loading of 0.02 wt%, air flow rate of 200 mL/min, foam height of 50 cm, and no added NaCl as electrolyte yield a carbon black recovery of 70% and a carbon black enrichment ratio of about 3.5.

To purify the as-prepared SWNTs obtained by disproportionation of CO gas over Co-Mo/SiO_2 catalyst, a first step of the silica removal by concentrated NaOH and a second step of the recovery of NaOH-treated SWNTs by froth flotation were studied. In order to achieve a high removal efficiency of froth flotation, a surfactant concentration of 0.75 times the CMC should be selected to avoid silica entrainment to the top of the column whereas sonication time of 3 h during the silica dissolution step, a sample loading of 1 mg/ml, an air flow rate of 100 ml/min, and a foam height of 22 cm yielded a maximum purity of about 78%, while the selectivity to SWNTs on the samples in the range of 71% indicates that most of SWNTs in the sample was recovered by combination of NaOH leaching and froth flotation technique.. This study has demonstrated that the combined silica dissolution and froth flotation technique can be applied to purify and concentrate the SWNTs synthesized by the disproportionation of CO over Co-Mo/SiO_2 catalyst without damage the physical structures of SWNTs.

Finally, this research showed that the production of single-walled carbon nanotubes by catalytic decomposition of carbon-containing gas over heterogeneous catalyst and its purification by froth flotation can be selected as an alternative way to produce SWNTs in commercial scale.

8.2 Recommendations

In this research, the growth mechanism SWNTs on Co-Re/SiO_2 catalyst is not clearly understood. More characterizations should be conducted in the future work. In the second study, the catalysts that were found to be active in SWNTs synthesis should be studied by observing the effects of operating condition to maximize the SWNTs production. Ultimately, the separation efficiency and throughput in froth flotation operation may be improved by changing surfactant, using mixed surfactant, and using continuous froth flotation system.