Synthesis of MWCNTs on $\text{CuSO}_4/\text{Al}_2\text{O}_3$ using chemical vapor deposition from methane

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Carbon nanotubes (CNTs) can be produced on a large scale by chemical vapor deposition (CVD) involving supported metal catalysts such as Fe, Ni, Co, and Mo, etc. [1,2]. Deck and Vecchio have recently shown that the carbon solubility in a metallic catalyst should be limited in the range of 0.5–1.5 wt.% carbon in order for the successful preparation of CNTs. In this regard, copper is expected to be catalytically inactive, due to its extremely low carbon solubility [2]. However, we found that multi-walled carbon nanotubes (MWCNTs) could be produced in high yield by catalytic decomposition of methane using a copper catalyst especially, when CuSO_4 was used with γ -alumina as the support. The catalytic activity of $\text{CuSO}_4/\text{Al}_2\text{O}_3$ reported herein is notably different from those involving other metals.

The $\text{CuSO}_4/\text{Al}_2\text{O}_3$ catalyst was prepared by impregnating γ - Al_2O_3 with an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.9%, Aldrich). The synthesis of CNTs was carried out in a fixed bed quartz tube reactor (1 cm outer diameter). The catalyst (50–100 mg) was loaded into the reactor and treated with a stream of He gas for 1 h at various temperatures (600–1100 °C). A mixture of CH_4/He in a ratio of 3/1 was introduced at a flow rate of 40 mL/min at desired temperatures for CNT synthesis.

Fig. 1 shows the catalytic activity of 5 wt.% $\text{CuSO}_4/\text{Al}_2\text{O}_3$ at different temperatures for the synthesis of CNTs. The growing of CNTs starts at about 600 °C and reaches to a maximum of rate at about 800 °C, then drops gradually to nearly zero, when temperatures are higher than 1000 °C. The temperature-dependent catalytic activity of Cu catalyst is quite different from those of Fe, Co and Ni, etc., where the growing rate of CNTs increases with the increasing of temperatures.

The effect of reaction time on the yield of CNTs on $\text{CuSO}_4/\text{Al}_2\text{O}_3$ at 800 °C is shown in Fig. 2. The yield was

calculated by the weight increment ratio (%) of carbon soot relatively to the weight of the catalyst. Thermogravimetric analysis suggests that the carbon soot produced on the catalyst surface contains 70% MWCNTs and 30% amorphous carbons [3]. The initial yield of carbon soot increases rapidly, but reaches to a plateau in about 60 min. The formation rate is about 4.2 g/g CuSO_4 per hour, which is quite good compared with those produced by catalytic CVD. The formation rate of CNTs on copper catalyst drops to a barely detectable level, when $\text{Cu}(\text{NO}_3)_2$ was used as the copper precursor instead of CuSO_4 on alumina surface. Fig. 3 depicts the SEM and TEM images of CNTs grown at 800 °C in 1 h on $\text{CuSO}_4/\text{Al}_2\text{O}_3$ and $\text{Cu}(\text{NO}_3)_2/\text{Al}_2\text{O}_3$ catalysts. The CNTs appeared to be a fish-bone type of carbon nanotubes. The TEM data suggest that the growth of CNTs on copper catalyst is consistent with a typical tip-growth mechanism, where carbon diffusion is followed by precipitation at the rear of the metal particles to form the body of the CNT. However, recognizing the complex catalytic reaction behavior, there is still much uncertain about the growth mechanisms of CNTs. We could not go beyond the consistent argument before a thorough study of how the hydrocarbon reacts with copper and how carbon diffuse in the metal is accomplished.

After being treated with a stream of He gas at temperatures between 800 °C and 1100 °C for 2 h the catalyst was analyzed by X-ray diffraction. As shown in Fig. 4 a copper diffraction pattern and a broad γ - Al_2O_3 diffraction pattern are observed after a treatment at 800 °C. The average diameter of copper estimated by the Scherrer equation without the correction of instrumental broadening is about 40 nm. An α - Al_2O_3 diffraction pattern develops gradually when the pretreatment temperatures are higher than 800 °C. γ - Al_2O_3 diffraction pattern fades away completely when the pretreatment temperatures are higher than 1000 °C.

The X-ray data afforded some clues for the understanding of the mechanism of the CNT synthesis on the copper catalysts. The special behavior of copper for catalyzing the CNT synthesis may correlate with the interactions between

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Fig. 1. The catalytic activity profile of 5% CuSO₄/Al₂O₃ versus temperature for the synthesis of carbon soot in CH₄/He (3/1) at a flow rate of 40 mL/min in 1 h.

Fig. 2. The yield of carbon soot produced on 5% CuSO₄/Al₂O₃ as a function of reaction time at 800 °C in CH₄/He (3/1) at a flow rate of 40 mL/min.

copper and γ -Al₂O₃. Copper and γ -Al₂O₃ are known to form a mixed oxide with a spinel-type structure [4]. Bonnelle et al. have demonstrated the critical importance of cuprous ions in an octahedral environment of the spinel structure for certain catalytic reactions [5]. This structure may also play an important role in catalyzing the methane decomposition and graphite formation reactions which facilitate the growing of CNTs. Chen et al. have demonstrated that α -Al₂O₃ does not adsorb or react with methane in any case [6]. High temperature treatment converts the γ -Al₂O₃ to α -Al₂O₃ and destroys the active spinel structure. Therefore a decrease of catalytic activity for CNT synthesis is observed.

The special behavior of copper for catalyzing the CNT synthesis reaction may also correlate with the interactions

Fig. 3. The SEM images of CNTs produced on (a) 5% Cu(NO₃)₂/Al₂O₃ (b) 5% CuSO₄/Al₂O₃ and (c) the HRTEM image of CNTs produced on 5% CuSO₄/Al₂O₃.

between copper and SO₄ ions on γ -Al₂O₃. The sulphate ion can interact with alumina and form a Lewis type super acidic site. The research on oxidative coupling of methane reveals that superacid catalyst presents enhanced activities to unlock the stable methane molecule and improves the conversion of methane into ethylene [7]. The superacidic species may also enhance the catalytic activity of copper in decomposition of hydrocarbon and facilitate the precipitation of carbon in forms of CNTs. The low activity of

Fig. 4. The XRD patterns of 5% $\text{CuSO}_4/\text{Al}_2\text{O}_3$ pretreated at (a) 800 °C, (b) 1000 °C, (c) 1100 °C in He for 2 h and (d) $\alpha\text{-Al}_2\text{O}_3$.

copper catalyst for the synthesis of CNTs when $\text{Cu}(\text{NO}_3)_2$ was used as the copper precursor supports this hypothesis. Fig. 5 shows the decomposition behavior of CuSO_4 on alumina surface. The catalyst has been treated with a stream of He at 400 °C before the temperature programmed decomposition experiment to remove the water from the sample. The maximum decomposition rate of CuSO_4 occurs at temperatures between 700 °C and 900 °C. Yang et al. also reported that the SO_4 superacidic species are decomposed at temperatures between 800 °C and 1000 °C [8]. Thus a lower catalytic activity of $\text{Cu}/\text{Al}_2\text{O}_3$ is observed after a higher temperature treatment.

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Fig. 5. Temperature programmed decomposition profile of 5% $\text{CuSO}_4/\text{Al}_2\text{O}_3$ with TCD as the detector. The catalyst was heated to 400 °C and then cooled to room temperature in a He gas flow before the temperature programmed decomposition experiment.

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