Highly Effective Carbon Nanotube Synthesis on C10 Co-MCM-41

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Introduction

There are many factors affecting SWNT quality and yield in the catalytic process, and the SWNT yield and quality are related to all these factors, which can possibly be improved by a systematic investigation of both catalyst and reaction conditions that have been over looked. Yield of SWNT has been a major barrier to applications that cannot be easily overcome; it is 5~6 wt% in most SWNT synthesis processes. High SWNT yield can be a significant benefit in a scaled-up process for a stable supply of SWNT. In order to achieve this goal, basic research focusing on the less studied factors in the SWNT synthesis need to be investigated.

The C10 MCM-41 having pore diameter of 1.8 nm measured by BJH method can accommodate more Co ions into the silica matrix without formation of surface oxides than C16 MCM-41, under the same Co loading.[1] Its reduction stability is much higher than that of C16 sample, showing very narrow temperature range for a full reduction, because of the faster ion migration at high temperature; therefore, most of Co ions can be utilized for SWNT production, resulting in a high yield. If one can utilize these properties of C10 Co-MCM-41 and modify the reaction and pre-treatment conditions, the limit of carbon yield may be improved.

In this study, C10 3 wt% Co-MCM-41 samples were synthesized and applied to the synthesis of SWNT using CO disproportionation to monitor catalytic behavior. The collected results will be analyzed to suggest a preliminary mechanism to explain the relationship between catalytic properties and high SWNT yield.

Materials and Methods

The C10 3 wt% Co-MCM-41 samples were synthesized under different soluble and colloidal silica ratios, and the initial pH of the synthesis solution as studied in the C16 samples earlier.[2] The physical properties were tested by nitrogen physisorption, showing the volume averaged structure indices, and the chemical properties were investigated by hydrogen temperature programmed reduction (TPR) and in-situ X-ray absorption experiment (EXAFS). The prepared C10 Co-MCM-41 samples were applied to the synthesis of SWNT using CO disproportionation to monitor catalytic behavior by comparing SWNT yield and characteristics measured by temperature programmed oxidation (TPO) using TG/DTG and Raman spectroscopy, respectively.

Results and Discussion

The optimum soluble and colloidal silica ratio, based on capillary condensation slope, for C10 Co-MCM-41 was 0.43 instead of 0.29 (C16's case). The samples synthesized using this ratio showed a systematic temperature shift under reduction as a function of the initial pH of the synthesis solution, as shown in Fig.1. As the initial pH increases, the metallic Co cluster size decreases due to the increasing reduction stability, which may affect the SWNT quality and yield under the same reaction conditions. The narrow reduction temperature range can be helpful to utilize incorporated Co ions. After reaction, all samples showed complete reduction and similar size of metallic clusters on average. Because of the possibility of re-oxidation at low linear velocity in CO disproportionation, the effect of linear velocity was investigated by fixing the gas flow rate while changing catalyst amount. As shown in Fig.2, the total carbon yield continued to increase until the reactant flow rate/catalyst amount=33 (ml/min·mg), showing 34 wt% of carbon with 96 % selectivity of SWNT. When the catalyst was reduced at the maximum reduction rate temperature, the carbon yield increased more, probably by minimizing CO consumption for reduction of unreduced Co ions. This suggests that most metallic clusters are utilized for SWNT production. The completely reduced metallic particles may be stabilized against the severe migration by the occlusion effect of amorphous silica, discussed earlier.[3]

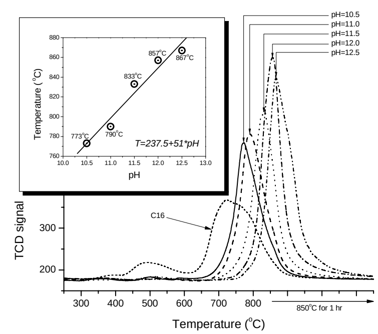

Figure 1. TPR results of the C10 Co-MCM-41 samples synthesized with different initial pH.

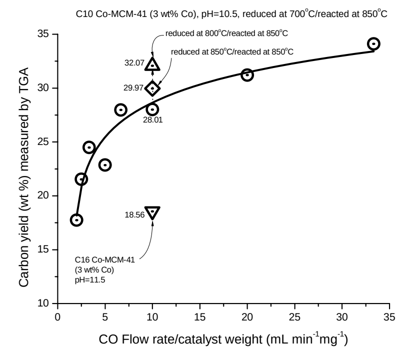

Figure 2. Effect of the linear velocity on the total carbon yield.

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Significance

This result can be a huge effect on the scaled-up SWNT production with maintaining the tube quality.

References

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3. Lim, S., Wang, C., Yang, Y., Ciuparu, D., Pfefferle, D. L., and Haller G. L., *Catal. Today*, in press.