

Large Particle Co-MCM-41 for Fluidized Bed Applications

Sangyun Lim, Fang Fang, Nan Li, Lisa D. Pfefferle, and Gary L. Haller*
Dept. of Chem. Eng., Yale Univ., P.O. Box 208286, NewHaven, CT 06520-8286, USA
*gary.haller@yale.edu

Introduction

A fluidized bed reactor is a promising approach for the catalytic growth of carbon nanotubes on a large scale to maintain a uniform bed temperature. However, the low bulk density of Co-MCM-41 is a major barrier to use in a fluidized bed reactor because of the small particle size with extremely high porosity, which results from the initial silica sources. In order to satisfy these requirements, metal ion incorporated MCM-41 with large spherical particles consisting of longer continuous pores inside the particles with uniform distribution of metal ions is required.

The concept of pseudomorphism may be a synthesis approach for large particle MCM-41 catalyst applications. Pseudomorphic synthesis of pure siliceous MCM-41 using large silica particles, 5 ~ 15 μm in diameter, was first introduced by Martin et al. in 2002,¹ applied to a separation medium,² and expanded to MCM-48.³ These processes are for pure siliceous mesoporous materials and utilize NaOH. However, for the application to MCM-41 as a catalytic material, metal ion incorporated MCM-41, sodium has a negative effect in the substitution of metal ions and catalytic reaction, as well as stability. Uniform distribution of metal ions through the pore surface is a key property in the metal ion incorporated MCM-41 compared to pure siliceous MCM-41.

In this study, therefore, a non-sodium process is introduced for the pseudomorphic synthesis of Co-MCM-41, which may be applied to a wide range of metal ions. The physical and chemical properties were investigated by temperature programmed reduction (TPR), nitrogen physisorption, and scanning electron micrograph (SEM) to suggest a set of preferred synthesis conditions for obtaining a successful Co-MCM-41 pseudomorph.

Materials and Methods

A non-sodium process was used to synthesize Co-MCM-41 following the detailed synthesis procedure described elsewhere.^{4, 5} Two different sizes of spherical silica, 15 μm (99.99 % SiO_2 , Kromasil, Eka Chem.) and 40 μm (99.9 % SiO_2 , Fluka), were used as parent silica, and the resulting samples were compared to the sample synthesized using fumed silica, Cab-O-Sil (Sigma-Aldrich, 0.2–0.3 μm). Effects of particle size and initial pH of the synthesis solution were investigated by assessing the reduction properties and stability, physical structure, and morphology using TPR, N_2 physisorption, and SEM, respectively. The fluidization test was performed with the parent silica (16–40 μm), and single wall carbon nanotubes (SWNT) were synthesized using large particle Co-MCM-41 in a fixed bed followed by characterization of produced SWNT.

Results and Discussion

Pseudomorphic synthesis of Co-MCM-41 using 15 μm and 40 μm spherical silica particles was successfully performed as shown in Fig.1. Autoclaving time and the initial pH of the synthesis solution were crucial factors to obtain non-ruptured morphology and complete transformation of parent silica large particles to the MCM-41 structure. These factors also

affected the distribution of Co ions in the MCM-41 structure, which is the key to some catalytic applications. The optimum autoclaving time and the initial pH were 4 days and 12, respectively. The initial pH adjustment of Co-MCM-41 synthesis solution affected the reduction stability by controlling Co ion location in the framework as well as hydrogen spillover on the surface. Finally, the successful application of these large catalytic particles in a fluidized bed synthesis of SWNT is a realistic prospect utilizing materials synthesized by the process described herein, based on the fluidization test of the parent silica as shown in Fig.2.

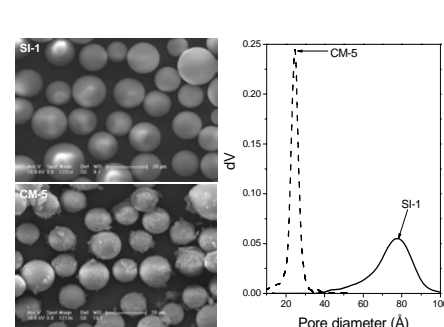


Figure 1. SEM images and pore size distribution showing pseudomorphic transformation of parent silica to Co-MCM-41.

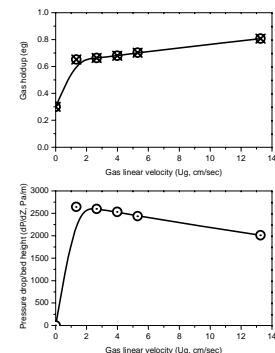


Figure 2. Fluidized bed test result of parent silica (16–40 μm).

Acknowledgement

We are grateful to DoE, Office of Basic Energy Sciences, Grant No. DE-FG02-01ER15183, and DARPA (Hexcel Corp. subcontract) for the financial support of this project.

Significance

This is the first case study for the application of MCM-41 catalyst in the fluidized bed, which is frequently used in industry for many catalytic gas phase reactions.

References

1. Martin, T.; Galarneau, A.; Di Renzo, F.; Fajula, F.; Plee, D. *Angewandte Chemie-International Edition*, *41*, 2590 (2002).
2. Martin, T.; Galarneau, A.; Di Renzo, F.; Brunel, D.; Fajula, F.; Heinisch, S.; Cretier, G.; Rocca, J. L. *Chemistry of Materials*, *16*, 1725 (2004).
3. Petitto, C.; Galarneau, A.; Driole, M. F.; Chiche, B.; Alonso, B.; Di Renzo, F.; Fajula, F. *Chemistry of Materials*, *17*, 2120 (2005).
4. Lim, S.; Yang, Y. H.; Ciuparu, D.; Wang, C.; Chen, Y.; Pfefferle, L.; Haller, G. L. *Topics in Catalysis*, *34*, 31 (2005).
5. Lim, S.; Ciuparu, D.; Chen, Y.; Yang, Y. H.; Pfefferle, L.; Haller, G. L. *Journal of Physical Chemistry B*, *109*, 2285 (2005).