行政院國家科學委員會補助專題研究計畫成果報告

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一、中文摘要

針對 MCM-41 中孔洞分子篩應用的研究，相關成果如下：

I、觸媒研究

主要在開發製備熱穩定性佳的 MCM-41 負載混合金屬氧化物以形成強酸性基，所選的混合金屬氧化物以 ZrO2/WO3 及 ZrO2/MoO3 為主，並與之前開發出來的 MCM-41 負載 SO42-/ZrO2 的超強酸之催化活性做比較；目前這方面的研究，仍在製備方法的改進與研發階段。

II 中孔徑分子篩之合成研究

在應用時，中孔徑分子篩的問題是其水熱穩定性加入鹽類可改進水熱穩定，我們徹底地研究合成時之離子效應。

III 表面修飾改質

在中孔徑分子篩之觸媒應用及離子吸附應用時，對表面修飾可使改質而增加疏水性或使均相觸媒異相化，我們成功地使 MCM-41 表面加上烷基，胺基及硫基化合物，我們並研究了一些陽離子之吸附效用。

關鍵詞：MCM-41 分子篩 觸媒 吸附

Abstract

In this year, we focus our attention on the synthesis control of mesoporous silica. This includes post-synthesis hydrothermal treatment, surface functionalization and counterion effects. The mesoporous materials can thus be synthesized with controls in pore size wall-thickness and morphology.

Key Words: MCM-41 molecular sieves, Catalysis, surface adsorption

成果報告：

1. Salt Effect in Post-Synthesis Hydrothermal Treatment of MCM-41

Postsynthesis hydrothermal treatment of MCM-41 porous silica provides a convenient method of pore expansion and improvement of its stability. The physical chemistry of the process is investigated by examining the effects of salt, aluminum, and water content on pore expansion. A hydrothermal treatment at 150 ^{o}C in water or salt solution leads to controlled pore expansion. The pore size varies with the kind

of anion of the salt and their concentrations. The salt effect follows the well-known binding strength Hofmeister series of anion for the cationic surfactant, $NO_3^->Br^->Cl^->SO_4^{2-}\sim F^-$. It is proposed that an equilibrium of distributing surfactants inside the MCM-41 channels and in solution controls the pore size upon varying the salts. The anion binds with surfactant molecules in solution to shift the equilibrium of surfactant/silicate binding leading to lesser surfactant and water in the pore and hence less pore expansion. The effect of ammonia hydrothermal treatment is to shift the equilibrium to stronger surfactant/silicate binding and thus more pore expansion. At neutral condition, the wall thickness varies inversely with respect to the pore diameter. The wall thickness variation agrees with a model of elastic deformation of the wall silica materials at high temperature.

2. A Direct Surface Silyl Modification of Acid-Synthesized Mesoporous Silica

A surface silyl modification and surfactant removal of acid-synthesized mesoporous silica process in a single step is investigated. The surfactant-silyl exchange process allows large amount of surface attachments of silanes.

3. Counterion Effect in Acid Synthesis of Mesoporous Silica Materials

The mesoporous silica materials with well-ordered hexagonal structure were synthesized under acid condition by using various acid sources HX. The induction period time for the formation of meso-structural precipitation increases in the lyotropic series: HNO_3 < HBr < HCl < H_2SO_4 under the same acid concentration. The induction rates are analyzed with a micelle-catalyzed reaction scheme. The order in induction time reflects the strength in counter-ion binding of X^-. Nitric acid with the highest binding strength counterion NO_3^- tends to form very long micelles. We have determined the counterion association constants and found the degree of counterion dissociation under synthetic condition in solution. The association is only partial during the early morphology-setting stage. HNO_3 is a suitable acid source for preparing hierarchical order silica ropes, which are consisted of silica fibers formed from parallel nano-sized channels. The elongation of the surfactant micelles and shearing flow are the controlling factors in the morphology. Temperature, acid concentration, surfactant chain length and the addition of polar solvent have strong influence on the morphology and nanostructure of the mesoporous materials under acid condition.

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