

CHAPTER II

LITERATURE SURVEY

In 1992, Mobil's scientists successfully synthesized a new family of mesoporous molecular sieves designated as M41S was reported. MCM-41, one member of this family, has uniform cylindrical pores in hexagonal arrangement and is produced using rod-like micelles of cationic surfactant molecules as a template. (S. Sathayanon, 2003) Generally, the original M41S family of mesoporous molecular sieves was synthesized by the combination of appropriate amounts of a silica source [e.g. tetraethylorthosilicate (TEOS), Ludox, fumed silica, sodium silicate], an alkyltrimethylammonium halide surfactant [e.g. cetyltrimethylammonium bromide (CTAB)], a base [e.g. sodium hydroxide or Tetramethylammonium hydroxide (TMAOH)], and water. The mixture was aged at elevated temperature ($\geq 100^{\circ}\text{C}$) for 24 to 144 hours, which resulted in a solid precipitate. The organic - inorganic mesostructured product was filtered, washed with water and air - dried. The product was calcined at about 500°C under a flowing gas to burn off the surfactant, to yield the mesoporous material. (S. Sathayanon, 2003)

Actually, there are 2 types of surfactants, supramolecular templating and liquid - crystal templating (LCT). Many research groups exploited this technique of supramolecular templating to produce not only mesoporous silicate and aluminosilicate materials, but also mesostructured metal oxides. The extension of this liquid - crystal templating (LCT) mechanism into the field of transition metal oxide synthesis represented a major step forward towards tailoring catalytic, electronic and magnetic properties of these redox - active materials. (S. Sathayanon, 2003)

Many researchers have tried to introduce other compound into the silica - based MCM-41 framework and iron is one of the significant transition metals which is celebrated.

Iron oxide has been deposited on M41S materials by incipient wetness of iron(III) nitrate solutions. All reports indicate the production of nanoparticles of Fe_2O_3 by this technique. UV-VIS spectroscopy results indicate that compared to the 4.1 eV band gap of bulk Fe_2O_3 , these nanoparticles display a significant quantum

size effect which yields a band gap reduced to 2.1 eV. Similar materials have been found active in the benzylation of benzene by benzylchloride, suggesting the formation of surface acid sites. This result would be in line with the observations, according to which the formation of Fe₂O₃ nanoparticles encapsulated in the pore lattice of MCM-41 and MCM-48 is accompanied by the substitution of some trivalent iron in the silicate framework. It was shown that very high Fe₂O₃ loading can be reached without crystallization or mesopore blockage (D. Trong On, 2003).

Fe-containing molecular sieve can be prepared using iron salts such as iron nitrate [Fe(NO₃)₃·9H₂O] as iron source. Modification of mesoporous molecular sieve (MCM-41, MCM-48 or HMS) by incorporation of transitional ions (Fe³⁺ ion for example) is well documented. The major problem with iron atoms is the formation of extraframework iron species during template removal by calcinations (N. Crowther, 2003). The synthesis of Fe-MMS with maximum incorporation of Fe (Si/Fe ratio of about 10) was performed in neutral conditions using primary amines. Using solvent extraction for the removal of the organic template (compared to conventional thermal treatment) preserves both the mesopore structure and the tetrahedral coordination of the cation in the framework (A. Tuel, 1999). These Fe-MMS were also found to be very active and selective catalysts (100%) for the benzylation of benzene. They were used for oxidation (hydroxylation of aromatic compounds and epoxidation of olefins), polymerization, reactions and oligomerization of propene (D. Trong On, 2003). Unfortunately, the activity of these oligomerization catalysts could not be enhanced by decreasing the Si/Fe ratio below 200 when prepared in basic medium (Y. Wang, 2001).

In the recent year, metal ion-incorporated MCM-41 has attracted much attention as oxidation catalyst. For example, Ti-MCM-41 was reported to catalyze various oxidation reactions with H₂O₂, but the epoxidation of cyclohexene could not proceed selectively over it with diluted H₂O₂ or Mn-MCM-41 showed high selectivity for the epoxidation of stilbene with *tert*-butyl hydroperoxide or TBHP (Q. Zhang, 2001) Recently, an iron-immobilized MCM-41 modified with organic silane exhibited activity in the oxidation of cyclohexane to cyclohexanol and cyclohexanone at 373 K with H₂O₂ (Carvalho A, 1999), The highest conversion of styrene over the Fe-MCM-41

via direct hydrothermal technique showed at 14% conversion over the catalyst of 1.1 wt% of Fe (Y. Wang, 2001). Moreover, the activity and efficiency of H_2O_2 increases with the metal content and reaction parameters such as temperature (B. Su, 2001).