

## CHAPTER II

### LITERATURE SURVEY

In 1992, a new family of mesoporous molecular sieves designated as M41S was successfully synthesized by Mobil's scientists. The initial members of the M41S family consisted of MCM-41 (hexagonal phase), MCM-48 (cubic  $Ia3d$  phase), and MCM-50 (a stabilized lamellar phase). MCM-41 has uniform cylindrical pores in hexagonal arrangement and is produced using rod-like micelles of cationic surfactant molecules as a template (Kresge *et al.*, 1992). After that, J.S. Beck *et al.* discovered MCM-41, formed by a mechanism in which surfactant liquid crystal phases are believed to serve as templates.

Chi-Feng Cheng *et al* (1995) reported that MCM-41 was synthesized with surfactant concentrations as low as, but not below, the critical micelle concentration, to provide the first direct proof that surfactant micelles indeed templated the synthesis. The micelle catalysis mechanism relies on electrostatic interaction at the micelle-silicate interface and the higher silicate concentration near the interface than in the bulk. Owing to their high hydrophilicity Ti-MCM-41 samples present a good catalytic behavior for oxidation in water-free media, when using organic peroxide as oxidants. This advantage was shown by T. Blasco. *et al.* Then J. Sudhakar Reddy *et al.* was successful using Ti-MCM-41 as a catalyst in the oxidation of propylamine to propionaldehyde oxime.

Titanium-containing MCM-41 which was prepared from the synthesis gel derived from  $Ti(OC_4H_9)_4$  and several Si sources was studied by K.A. Koyano, T. Tatsumi in 1997. Tetraethyl orthosilicate (TEOS), which is free from Al and Na, as a silica source, was used to incorporate titanium into the framework of MCM-41 without the formation of anatase. Ti-MCM-41 was applicable to the oxidation of bulky alkenes with  $H_2O_2$  or t-butyl hydroperoxide (TBHP) as an oxidant. The stability of Ti-MCM-41 against water was low, compared to pure-silica MCM-41.

Another source of titanium,  $(NH_4)_3[Ti(O_2)F_5]$ , was discovered by Thomas E.W. Nießen *et al*(1998). They synthesized titanium-containing MCM-41 that is an active catalyst in the oxidation of tran-1,2-cyclohexanediol, but are slightly active in

the ammoximation of cyclohexanone. Besides, the use of surfactant with increasing chain length as the template resulted in materials with an increasing mean pore size.

J.-Y. Piquemal *et al* (1999) reported that mesoporous molybdosilicate, [Mo]-MCM-41, molecular sieves with variable amounts of molybdenum (VI) were synthesized in acidic media from  $\text{MoO}_3$ , aqueous hydrogen peroxide and tetraethyl orthosilicate as the silicon source. This procedure avoids the formation of iso-(or hetero-) polyoxometalates and eliminates the need for careful control of the rate of hydrolysis of the metal precursors, e.g. alkoxides, sometimes involved in the syntheses of transition metal-containing mesoporous materials.

Michal Kruk and Mietek Jaroniec (1999) were interested in improve the pore size of MCM-41. The swelling properties of DMHA were confirmed by a successful synthesis of large-pore MCM-41 in mild conditions in the presence of DMHA and preparation of silicas with pore sizes up to 11 nm and extremely large-pore volumes up to  $2.4 \text{ cm}^3/\text{g}$  via re-structure of 3.5 nm. The reasons for the pore volume increased and surface area decreased during the pore size enlargement were discussed. Moreover, it was suggested that the unit-cell expansion in the direction perpendicular to the pore channels was accompanied by shrinkage of the structure in the direction parallel to the channels. The development of titanium-substituted derivatives of the mesoporous molecular sieves MCM-41 was also prepared by post-synthetic methods, as reported by W.S. Ahn *et al* (1999), using Ti-butoxide or titanocene grafting without destroying the mesopore structure. Ti-substituted mesoporous derivatives both prepared by hydrothermal and post-synthetic methods were catalytically active for the selective oxidation of 2,6-DTBP with  $\text{H}_2\text{O}_2$ .

In 2000, Asim Bhaumik and Takashi Tatsumi modified Ti-MCM-41 samples that were efficient catalysts in the epoxidation and oxidative cyclization using TBHP as oxidant under mild liquid phase reaction conditions. The oxidation activity increases four- to five folds by using TBHP as oxidant over that seen when using aqueous  $\text{H}_2\text{O}_2$ .

Several transition-metal-based, titania-loaded MCM-41 (Si/MeD80, titania content 25 wt%) materials were tested for the degradation of organics in visible light, as studied by Lev Davydov *et al.* (2001). The chromium-substituted MCM-41 was found to serve as the best support for titania to achieve the highest degradation rates

of formic acid, 2,4,6-trichlorophenol, and 4-chlorophenol. The change in the state of the catalyst during the reaction was observed for Cr-substituted molecular sieves, leading to its deactivation. The mechanism of the photodegradation in visible light on titania-loaded, transitionmetal-substituted MCM-41 was proposed.

Zhengping Li *et al.* (2002) studied on the dispersion of  $\text{MoO}_3$  onto the surface of mesoporous silica MCM-41 by means of thermal spreading, using different characterization techniques. XRD results showed that  $\text{MoO}_3$  was dispersed on the surface of MCM-41 and transformed into dispersed  $\text{MoO}_3$  species after thermal treatment of the mixtures of MCM-41 and  $\text{MoO}_3$  at 773 K for 24 h.

A. Bhattacharyya *et al.* (2004) studied photocatalytic efficiency of supported  $\text{TiO}_2$  catalyst on three types of adsorbents compared with that of bare  $\text{TiO}_2$  produced by sol-gel method and commercially available Degussa-P25 catalyst. The supported catalysts effectively removed an azo-dye orange II from solution, and the rate of degradation was significantly better than that of bare  $\text{TiO}_2$  (sol-gel) and Degussa-P25. The performance improvement can be attributed to the high surface areas of the adsorbent used, crystallinity and particle size of deposited  $\text{TiO}_2$ . All three supported catalysts exhibited comparable overall removal efficiency of orange II, although  $\text{TiO}_2$ -MCM-41 and  $\text{TiO}_2$ -b-zeolite were better photocatalysts than  $\text{TiO}_2$ -montmorillonite while adsorption of orange II was maximal on  $\text{TiO}_2$ -montmorillonite. The performance of the supported catalysts depended significantly on the nature of the substrate used.

Mo-MCM-41 was found to possess three different types of Mo-oxide species by Shinya Higashimoto *et al.* (2005). The concentrations of which were dependent on the Mo content were a highly dispersed tetra-coordinated monomeric molybdate, a tetra-coordinated dimeric and/or oligomeric molybdate, and a hexa-coordinated polymeric molybdate. Moreover, the tetra-coordinated molybdate species was observed to play a major role in the photocatalytic reduction of NO in the presence of CO to form  $\text{N}_2$  and  $\text{CO}_2$ .

L.A. Rios *et al.* (2005) found that the use of molecular sieves, like MCM-41, as a titanium support, did not offer any additional advantages other than high surface area for the epoxidation of plant oils. The presence of pores was not necessary. The results suggested that the reaction occurred over a large external surface area. The

epoxidation was also carried out with a non-crystalline amorphous Ti-SiO<sub>2</sub>. The important issue here is to have the titanium center finely dispersed over a relatively high surface area.