CHAPTER I

INTRODUCTION

Since 1992 after mesoporous molecular sieves in M41S family were discovered by Mobil's group [Kresge C.T. *et al.*, 1992; Beck J.S. *et al.*, 1992], these materials have attracted remarkable attentions due to its high surface area, ordered pore structure array, and narrow pore size distribution [Shao Y. *et al.*, 2005]. There are three categories of M41S divided by the different arrays, viz. hexagonal (MCM-41), cubic (MCM-48), and lamellar (MCM-50) [Sayari A., 1996; Vinu A. *et al.*, 2003]. Among them, MCM-48 is a more attractive candidate as a catalyst, catalyst support, adsorbent, or template for synthesis of advanced nanostructures, probably owing to its unique three-dimensional pore structure. The cubic MCM-48 indexed in the space group of *Ia3d* is the most interesting in terms of catalytic activity because it has a three-dimensional pore structure which reduces the diffusion limitation and avoids the pore-blocking of the catalysts [Monnier A. *et al.*, 1993].

Although MCM-48 is a more attractive candidate as a catalyst support or adsorbent than MCM-41, its success is curtailed by the lengthy reaction times and rigorous conditions required for its synthesis. The cubic MCM-48 is an intermediate during the transformation from hexagonal to lamellar phases; thus, the synthesis conditions must be carefully controlled. Silica sources are also found to affect the MCM-48 formation, as studied by Xu et al. (1998), resulting in different silica structures. Therefore, most researchers have mainly focused on MCM-41 rather than MCM-48 [Huo Q. *et al.*, 1996; Gallis K.W. *et al.*, 1997; Corma A. *et al.*, 1998; Ryoo R. *et al.*, 1999; Sayari A., 2000; Xia Y.D. and Mokaya R., 2003]. Furthermore, a high surfactant amount and additives are required to obtain the cubic *Ia3d* MCM-48 mesoporous structure. To date, many researchers have tried to minimize the surfactant amount in many ways, using such means as organic additives [Kumar D. et al., 2001; Kim T.W. *et al.*, 2010] or salts (i.e. NaF and Na_2SO_4) [Wang L. *et al.*, 2006; Wang L. *et al.*, 2009]. Generally, to obtain MCM-48, the most widely used raw materials are CTAB as a surfactant, NaOH as a catalyst, and tetraethylorthosilicate (TEOS) as a silica source, using conventional autoclave heating for several days. According to the materials safety data sheets (MSDS), however, TEOS presents significant handling problems due to such factors as high toxicity and moisture sensitivity. In this research, we introduce another source of silica known as silatrane. Silatrane can be easily synthesized from inexpensive and commercially available starting materials, namely, silicon dioxide and triethanolamine, in ethylene glycol solvent [Phiriyawirut P. *et al.*, 2003; Charoenpinijkarn W. *et al.*, 2001]. One unique characteristic of silatrane is a moisture stability lasting up to several weeks, thus allowing for control of the hydrolysis rate during sol–gel processing.

In previous works, we successfully synthesized many microporous [Sathupanya M. *et al.*, 2002; Sathupanya M. *et al.*, 2003; Phonthammachai N *et al.*, 2003; Phiriyawirut P. *et al.*, 2005] and mesoporous [Thanabodeekij N. *et al.*, 2005; Thanabodeekij N. *et al.*, 2006; Mintova S. and Cejka J., 2007; Perez-Ramirez J. *et al.*, 2008] zeolites via sol–gel process, using moisture stable metal alkoxides for example silatrane, alumatrane, cerium glycolate, zirconium glycolate as the precursors. In this work, we systematically studied the effects of crystallization temperature, crystallization time, surfactant concentration, amount of NaOH, and silica source on the product structure to obtain the optimum synthesis conditions of MCM-48.

Since the materials themselves possess weak acidity and are deficient in necessary redox ability, thus exhibit low activity when directly used as catalyst [Vinu A. *et al.*, 2006]. To obtain materials with high catalytic performance, many attempts have been trying to incorporate hetero-element, such as Cr [Sakthivel A. *et al.*, 2001; Shao Y.*et al.*, 2008], Ce [Shao Y. *et al.*, Wang L. *et al.*, 2006; Wangcheng Z.*et al.*, 2008] or Ti [Thanabodeekij N. *et al.*, 2005; Yuan S. *et al.*, 2008] to the silicate framework so as to impart acid and/or redox properties of the materials [Kruk M. and Jaroniec M., 1999]. Thus, this work is also focused on the metal loaded MCM-48 i.e. Cr-MCM-48, Ce-MCM-48 and Ti-MCM-48 using moisture stable metal alkoxide precursors via sol-gel process. The catalytic activity of metal loaded MCM-48 is also studied.