CHAPTER I
INTRODUCTION

The important application of silatrane is used as a precursor in the synthesis of mesoporous silica via the sol-gel technique. Generally, most researchers use tetraethylorthosilicate (TEOS) as a silica source; however, several drawbacks has been identified for TEOS, such as high toxicity and moisture sensitivity, causing too fast hydrolysis rate. Thus, the rate needs to be retarded using excess ethanol. In contrast, silatrane has hydrolytic stability in air lasting up to several weeks, so the hydrolysis rate can be controlled in the absence of ethanol. Therefore, silatrane is a more attractive silica precursor to synthesize mesoporous materials because of its simple and easy synthesis from commercially available and low cost starting materials and the aforementioned advantage over TEOS. (Longloilert *et al.*, 2011; Puri *et al.*, 2011)

Porous materials have been studied with respect to applications as catalysts and catalyst supports. IUPAC classifies porous materials into three catagories: microporous (pore size < 2 nm), mesoporous (2–50 nm) and macroporous (> 50 nm) materials. Microporous materials present mass transfer limitations due to the large reactant. These limitations can be overcome with mesoporous materials which allow the large molecule to enter inside the pore. Order mesoporous materials of the M41S family were first successfully synthesized by Mobil researchers. These materials exhibit large specific surface area and uniform pores with a narrow size distribution. According to the different arrays, M41S are classified in three classes. They are hexagonal (MCM-41), cubic (MCM-48) and unstable lamellar (MCM-50) phases. (Taguchi *et al.*, 2005; Logar and Kaučič, 2006) After the discovery of M41S materials. researches on mesoporous family have been developed, such as TUD-1 materials. Both MCM-48 and TUD-1 exhibit three-dimensional pore system which can avoid pore blocking and allow faster diffusion of reactant than one-dimensional pore of MCM-41. Common properties of TUD-1 are an interconnecting 3D pores, tunable mesopore size distribution (25–250 Å), high surface area (400–1000 m^2/g), thicker mesopore walls and hydrothermal stability. In addition, the sponge-like TUD-

1 is an inexpensive and environmental friendly as it is non-surfactant structure directing agent. (Angevine *et al.*, 2009; Aquino and Maschmeyer, 2009) Nevertheless, pure silica porous material is of limited use for catalytic applications due to the lack of catalytic active sites. Recently, many researchers reported that the incorporation of heteroatoms, such as Ce, Fe, Cu, and Ti (Shao *et al.*, 2005; Prasad *et al.*, 2008; Pachamuthu *et al.*, 2013), into the framework of mesoporous materials can generate acid and redox active sites. Supported bimetallics, namely Al-Fe, Zr-Fe, Ce-Al, and Ce-Mn, are very interesting materials since one metal can modify the structural and redox properties of the other. (Molina *et al.*, 2006; Kalita *et al.*, 2007; Park *et al.*, 2007) Consequently, bimetallic catalysts usually improve catalytic activity, selectivity, and stability of the monometallic catalysts.

In last decade, Wongkasemjit's research group has developed microporous and mesoporous material, namely zeolites, SBA-15, MCM-41, MCM-48, etc., via sol-gel process. Because of hydrolytic stability of metal alkoxides, such as silatrane, alumatrane, cerium glycolate, tris(glycozirconate), lead glycolate, titanium glycolate, and molybdenum glycolate, they were applied for synthesis of porous materials. The 'oxide one-pot synthesis' (OOPS) process was used to synthesize these metal alkoxides used as precursors for the synthesis of heterogeneous mesoporous catalysts. (Longloilert *et al.*, 2011; Sathupunya *et al.*, 2004; Samran *et al.*, 2011; Ksapabutr *et al.*, 2004; Tangboriboon *et al.*, 2006; Thanabodeekij *et al.*, 2005, 2006, 2007)

The purpose of this work is to synthesize bimetallic three-dimensional mesoporous materials via sol-gel technique using silatrane as a silica precursor. The catalytic applications of metal loaded MCM-48 and TUD-1 are investigated. The effects of metal loading, amount of the oxidant, reaction temperature, and catalysts mass are also studied. In addition, hydrothermal stability, leaching, and reusability are observed in this study, as well.