CHAPTER I
INTRODUCTION

Porous materials have been successfully used as heterogeneous catalysts in many industries for decades. According to IUPAC notation, they are classified into 3 kinds by their pore diameter (d): micro-, meso-, and macro-porous with $d < 2.0$, $2.0 \leq d \leq 50$, and > 50nm, respectively (Rouquerol *et al.*, 1994). Mesoporous materials are more preferred for its highly ordered mesostructure, high surface area, and larger pore size than microporous materials, thus allowing diffusion and adsorption of higher molecular weight molecules (Angevine *et al.*, 2008). Therefore, these materials are useful for catalysis in petrochemical industrial. Besides, they are widely applied in drug control delivery, biosensors, biofuel, sorption, and membrane separation. Typical compounds of mesoporous materials contain silica, alumina, carbon and transition metal oxides (Rahmat *et al.*, 2010).

In 2001, researchers from Lummus Technology and the Delft University of Technology discovered a new mesoporous material originally emphasized on silica version, called TUD-1, which is a three-dimensional amorphous structure of random and interconnecting pores (Jansen *et al.*, 2001). Unlike most other mesoporous materials, TUD-1 has more effective properties. For instance, it has a high surface area (400–1000 m^2/g), an excellent hydrothermal stability, a tunable pore size, and a better accessibility of other molecules to diffuse into and out of them making the material an ideal starting point for catalyst development (Angevine *et al.*, 2008; Telalovic *et al.*, 2009).

The original synthesis method involves tetraethylorthosilane (TEOS) as the monomeric silica source mixing with triethanolamine (TEA) and optionally tetraethylammonium hydroxide (TEAOH). TEAOH acts as a template while TEA acts as co-template for both meso- and some micropore formation. Moreover, TEAOH generates a basic environment to accelerate TEOS hydrolysis (Angevine *et al.*, 2008).

According to the materials safety data sheets (MSDS), however, TEOS shows significant handling problems due to its high toxicity and moisture sensitivity.

In the last decade, Wongkasemjit's research group introduces another source of silica known as silatrane, which can be easily synthesized from inexpensive and commercially available starting materials, namely, silicon dioxide and TEA, in ethylene glycol (EG) solvent. One unique characteristic of silatrane is the moisture stability lasting up to several weeks, thus allowing for control of the hydrolysis rate during sol–gel processing (Longloilert *et al.*, 2011).

Instead of using TEOS as the silica source, many types of mesoporous materials can be easily and directly synthesized via sol-gel methodology using silatrane as silicon source (Thanabodeekij *et al.*, 2005; Tanglumlert *et al.*, 2007; Samran *et al.*, 2011; Longloilert *et al.*, 2011). This silatrane precursor generates TEA after hydrolysis, resulting in another structural directing agent. Thus, it should be another advantage of using this precursor.

However, one drawback of the mesoporous silicates is the few catalytic active sites. The incorporation of metals including most of the transition metals and some main group elements, such as boron, gallium, and indium etc., into the frameworks of mesoporous materials can modify the composition and improve catalytic activity of the materials (Wu *et al.*, 2012). Generally, transition metals can be used to incorporate into mesoporous materials by a post-synthetic ion-exchange treatment (impregnation) or by direct framework substitution by the addition of transition metal cations into the synthetic gel (Kustrowski *et al.*, 2005). In this research, the latter method was emphasized to synthesize bimetallic incorporated TUD-1. In addition, oxidation of phenol was selected as a model reaction for catalytic efficiency study due to its oxidation products, viz. catechol (CAT), hydroquinone (HQ) and benzoquinone (BQ), widely used as important precursors in the many valuable chemicals production. For instance, catechol is the precursor in the production of pesticides, perfumed, and pharmaceutical products whereas hydroquinone is used in rubber antioxidants, herbicides, and dyestuffs (Adam *et al.*, 2013). Furthermore, benzoquinone is also an important precursor in hydroquinone production and used as a polymerization inhibitor, as an intermediate in the production of a variety of substances, such as rubber accelerators and oxidizing agents (IARC, 1977). In many researches, titanium and iron are widely loaded into many mesoporous silica and tested as catalysts for this reaction, including Ti-MSU

(Song *et al.*, 2011), Ti-SBA-12, Ti-SBA-16 (Kumar *et al.*, 2013), Fe-MCM-48 (Zhao *et al.*, 2010), Fe-MCM-41 (Choi *et al.*, 2006), and Fe-HMS (Liu *et al.*, 2008).

The incorporation of bimetallics can modify the surface properties more effectively than those monometallics incorporated (Wu *et al.*, 2012). Thus, the objectives of this work are to synthesize bimetallic Fe/Ti loaded TUD-1 via the sol-gel technique using silatrane as a precursor, and to study catalytic activity on oxidation of phenol. Many factors are studied to find the optimum condition, such as reaction temperature, reaction time, amount of metals loaded, amount of catalyst, and molar ratio of reactants. Moreover, leaching, recycling and thermal stability of the catalyst and photocatalytic reaction will be also studied in this work.