CHAPTER I
INTRODUCTION

Porous materials have been used as heterogenous catalystss in many industries for decades. In general, they are referred to microporous (< 2 nm) and macroporous (> 50 nm) materials which play more important role in catalysis. However, many industrial scientists have been searching for the materials which have intermediate pore sizes between the microporous and the macroporous range. Such materials are called "mesoporous" materials which have pore diameters between 2–50 nm. Mesoporous materials have been studied as catalyst supports of many applications. These materials show the uniformity of pore size with a narrow pore size distribution and large specific surface area. In these days, the demands for porous materials are concerned not only with the pore sizes, pore size distribution, and surface area, but also with the chemical interaction with adsorbates. The demands include mesoporous materials having weak solid acidity, and porous materials having hydrophobicity. The demands on the materials are diverse and mesoporous materials using new materials are required. Typical mesoporous materials contain some kinds of silica and alumina that have well-sorted fine mesopores. Since the new mesoporous silicate and aluminosilicate materials of the M41S family were discovered by researchers of Mobil in 1980, they have opened a new field in the world of catalyst.

The M41S materials can be categorized into three classes: (1) MCM-41, one-dimensional (1D), hexagonal structure, (2) MCM-48, a cubic structure with three-dimensional (3D) and two, nonintersecting pore systems, and (3) MCM-50, a layered structure with silica sheets between the layers (Angevine, *et al.*, 2008). The order in the structure is derived from the channel arrangement.

After the first synthesis of the M41S materials was published, TUD-1 was discovered in 2001 at the Technische Universiteit Delft by Jansen *et al.* TUD-1 is the siliceous mesoporous material having the 3D randomly amorphous structure (Fig. 1.1 and 1.2). Generally, TUD-1 has more effective properties, such as high surface area (400–1000 m^2/g), interconnecting 3D pores that allow other molecules to diffuse into and out of them to make the material an ideal starting point for catalyst development, hydrothermal stability, and tunable porosity. TUD-1 can be directly synthesized via sol-gel methodology using silatrane as silicon source, as used to develop other materials by Wongkasemjit's research group (Thanabodeekij, *et al.*, 2006, Tanglumlert, *et al.*, 2007, Bussaraporn, *et al.*, 2011, Longloilert, *et al.*, 2011).

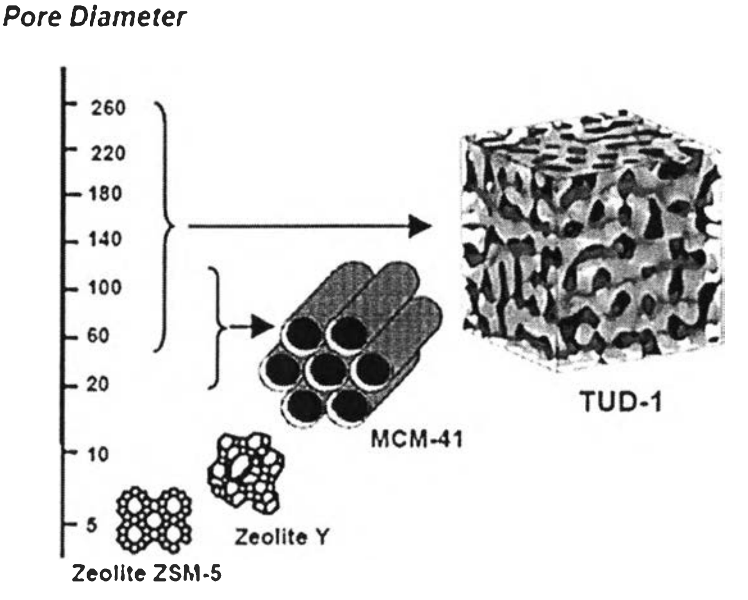

Figure 1.1 Pore diameter of TUD-1 in comparison to some major molecular sieves, ZSM-5, Zeolite Y, and MCM-41. Note that the pore diameter of TUD-1 can be varied from 40 to 250 Å. (Angevine, *et al.*, 2008).

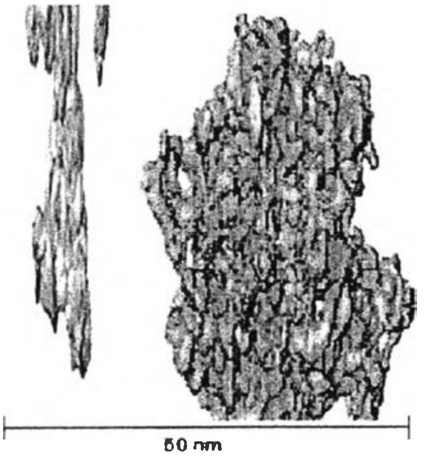

Figure 1.2 3-D TEM showing the irregular pore structure of TUD-1 (Angevine, *et al.*, 2008).

Moreover, TUD-1 with its three-dimensional sponge-like structure and other properties are ideal for being used in the catalysis field. Particularly, metal loaded TUD-1 has been proven to be a very versatile and stable catalyst for use in many reactions as other mesoporous materials.

Mesoporous materials have widely been used in many reactions as support for metal catalyst. One of these interesting reactions is Suzuki–Miyaura cross-coupling initially published in 1981 (Suzuki *et al.*, 1999). It is a cross-coupling reaction of organoboron compounds with organic halides, resulting in the formation of carbon-carbon bonds. The main product of this reaction is a biaryl compound, which is a significant intermediate product of biological active compound and often found in the arrangement of pharmaceuticals, herbicides, natural products and engineering materials (Cepanec *et al.*, 2004). The Suzuki-Miyaura cross-coupling reactions are usually formed using any arylboronic acid and arylhalide as the substrates (Gürbüz *et al.*, 2010). Due to the versatile processing capabilities and the ease of product/catalyst separation of such reactions, the immobilized catalysts can offer many advantages for industrial applications (Gürbüz *et al.*, 2010).

The objectives of this work are to synthesize TUD-1 and Pd-loaded TUD-1 mesoporous materials via the sol-gel technique and impregnation technique, respectively, using silatrane as a precursor, and to investigate the catalytic activity of Pd-TUD-1 on the Suzuki-Miyaura coupling reaction.