

CHAPTER I

INTRODUCTION

Aluminophosphate molecular sieves, known as $\text{AlPO}_4\text{-}n$ (n refers to a distinct structure type) and built from alternating $(\text{AlO}_4)^-$ and $(\text{PO}_4)^+$ tetrahedra linked together to form a neutral framework (Wilson *et al.*, 1982), are useful in a number of applications; in particular as catalysts and catalyst supports, ion exchange, and adsorption. The aluminophosphate frameworks can be modified by other elements, e.g. the incorporation of silicon results in silicoaluminophosphate molecular sieves, SAPO (Jhung *et al.*, 2004), the addition of metal cations (M) yields metaloaluminophosphate, MAPO (Lee *et al.*, 2003; Saha *et al.*, 2005) or metalosilicoaluminophosphates, MeAPSO (Nomura *et al.*, 1998). These provide a mechanism for generating bronsted acidity, ion exchange capacity, and enhancing hydrophilicity. These properties of AlPO_4 and SAPO, including their transition metal doped materials, have attracted much attention as heterogeneous catalysts for oxidation, methanol conversion, ethylene dimerization, etc.

Among them, a well known $\text{AlPO}_4\text{-}5$ zeotype with an AFI type framework has one-dimensional 12-membered-ring channels parallel to the c -axis with a pore diameter in micropore region of 0.73 nm (Wilson *et al.*, 1982). The framework of SAPO-5 zeotype is also similar to that of $\text{AlPO}_4\text{-}5$ with the AFI structure. AFI has attracted much attention due to its zeolitic properties, excellent thermal stability, use in catalysis, and potential applications, such as host matrix to organize dye molecules for nonlinear optics (Caro *et al.*, 1992).

The aluminophosphates are generally prepared under conventional hydrothermal heating conditions (Wan *et al.*, 2000; Gua *et al.*, 2005; Jiang *et al.*, 2006) with a reaction time ranging from several hours to several days. However, a new synthesis technique combining hydrothermal and microwave heating was also employed for the preparation of microporous $\text{AlPO}_4\text{-}5$ zeotype (Girmus *et al.*, 1995; Du *et al.*, 1997; Fang *et al.*, 1997; Mintova *et al.*, 1998; Jhung *et al.*, 2004) due to a reduction of the crystallization time (Laha *et al.*, 2006). Moreover, the microwave heating apparently uniform crystal size distribution (Kodaira *et al.*, 1999), providing

a higher phase purity (Mintova *et al.*, 1998) and phase selective crystallization by getting rid of unstable materials (Yoon *et al.*, 2005). These results are from higher heating rate, faster dissolution of the gel and a more homogeneous heating by microwave irradiation, as compared with conventional heating.

Although the microporous $\text{AlPO}_4\text{-5}$ and SAPO-5 have been developed by several groups, its micropore still causes diffusion limitation. Recently, a new family of crystalline zeolitic materials, so-called mesoporous zeolite single crystals, was reported to overcome this problem (Jacobson *et al.*, 2000; Naydenov *et al.*, 2005; Egeblad *et al.*, 2007). These materials combine the benefits of mesoporous molecular sieves and zeolites. The mesopore improves the mass transfer to and from the active sites. These mesoporous zeolites are found to enhance catalytic properties, as compared to conventional zeolites (Christensen *et al.*, 2003; Xiao *et al.*, 2006).

Many metal alkoxide precursors have been synthesized by Wongkasemjit and coworkers, namely, alumatrane (Opornsawad *et al.*, 2001), silatrane (Piboonchaisit *et al.*, 1999), titanium glycolate (Phonthamamachai *et al.*, 2002), etc., directly from inexpensive and available compounds using ethylene glycol as solvent via the "Oxide One Pot Synthesis (OOPS)" process. This reaction gives highly pure metal alkoxides and moisture stable that have been successfully applied for synthesizing various zeolites, such as Na-A (LTA) (Sathupunya *et al.*, 2003), MFI (Phiriyawirut *et al.*, 2003), K-H (Sathupunya *et al.*, 2004), Li-Zeolite (Sathupunya *et al.*, 2004), VS-1 (Phiriyawirut *et al.*, 2005), and MCM-41 (Thanabodeekij *et al.*, 2006).

Thus, the aim of this work was to synthesize mesoporous $\text{AlPO}_4\text{-5}$ and SAPO-5 using atrane precursors via microwave technique. Triethylamine (TEA) was used as a structure-directing agent. In addition, the synthesis mixture without adding TEA was also carried out. Additionally, Pt metal was loaded onto these materials to investigate the efficiency of these catalysts on the preferential oxidation (PROX) of CO in H_2 -rich gas.