CHAPTER I

INTRODUCTION

Metal alkoxides are of interest in the past few years for production of advanced materials via sol-gel process. The sol-gel process involves in both hydrolysis and condensation reactions. Thus, careful control of both reactions, depending on hydrolytic property of those metal alkoxides, provides desired size and morphology of metal oxides, meaning that it is possible to design materials having tailored morphology. Moreover, it is well known that the sol-gel process eliminates impurities commonly found in conventional process because of high purity of precursors used in the process.

Metal alkoxides are also found to be very useful for producing mesostructured materials. In recent years, there have been dramatic advances in the concept of molecular sieves, exhibiting uniform pore sizes. Generally, pores are classified according to pore diameter, as follows: diameters of micropores, mesopores and macropores are less than 2 nm, between 2 and 50 nm and greater than 50 nm, respectively (Beck *et al.*, 1992). Amorphous mesoporous materials represent an important class of porous inorganic solids, having no long-range order and usually having a wide distribution of pore sizes whereas microporous molecular sieves have a crystalline structure with a very narrow pore size distribution. It is generally presumed that mesoporous materials with uniform pores would have wider utility in catalysis. Therefore, considerably synthetic effort has been devoted to develop frameworks with pore diameters within the mesoporous range, and atrane precursors are found to provide a very versatile route to ordered mesoporous materials. Previously, the syntheses of atrane complexes were carried out by means of transesterification reaction, starting from alkoxy derivatives in non-aqueous dried solvents under an inert atmosphere. Many studies showed that mesoporous materials were synthesized by mixing the atrane precursor with a surfactant in alkaline aqueous solution (Haskouri *et al.*, 2001; Haskouri *et al.*, 2002; Cabrera *et al.*, 2000). Not only the procedure is quite complicated, but also the alkoxide precursor used for the atrane complex synthesis is commercially expensive (Verkade, 1993; Pinkas, 1993).

Owing to large specific surface area ($>1,000$ m^2g^{-1}) and mesoporous property of MCM-41, many scientists have made use of MCM-41 as support material for heterogeneous catalysts to provide access to large molecules and alleviate diffusion problems, which are frequently encountered in microporous materials, such as zeolites (Barton *et al.*, 1999; Xiu *et al.*, 1996). They also tried to introduce a second cation, such as, a transition metal, into the silica-based MCM-41 framework, and used them as effective catalysts for various kinds of reactions. MCM-41 framework structure is flexible, as compared to crystalline zeolites, thus allowing various kinds of metal to be incorporated into the framework without destroying its basic structure when the preparation conditions are carefully controlled. Vanadium or titanium-substituted MCM-41 materials were found to be very active catalysts in the selective oxidation of hydrocarbons using H_2O_2 in liquid phase reaction, especially, for larger molecules (Smarsly *et al.*, 2001). More generally, it is now recognized that a number of the most promising oxidation catalysts is characterized by well-defined active sites containing one or only a few metal centers on the surface of an oxide support. Typically, these active sites are associated with a specific inorganic structure, giving rise to the desired catalytic properties.

During the last few years, Wongkasemjit and coworkers (2001-2004) synthesized moisture stable metal alkoxides, namely, silatrane, alumatrane, cerium glycolate, zirconium glycolate, titanium glycolate, tin glycolate and molybdenum glycolate, directly from inexpensively corresponding metal oxides using ethylene glycol solvent via the "Oxide One Pot Synthesis (OOPS)" process. The reaction gives highly pure metal alkoxides. Both synthesized silatrane and alumatrane have been successfully used for syntheses of various zeolites, such as, LTA (Sathupanya *et al.*, 2002), ANA, GIS (Sathupanya *et al.*, 2003) and MFI (Phiriyawirut *et al.*, 2003). Furthermore, the sol-gel process of titanium glycolate has led to the formation of high surface area TiO_2 having highly photocatalytic property. In addition, those alkoxide precursors are appropriate for preparation of materials in others forms, such as, ceramic powder, ultra-fine particle, fibres, thin film and monolith, etc. Mixed oxides and advanced ceramics were also prepared using those precursors.

Thus, our major aim is to study a novel synthetic route to remarkably high surface area MCM-41, Ti-MCM-41 and Mo-MCM-41 using atrane precursors using

hexadecyltrimethyl ammonium bromide (CTAB) as a template. Influences of variables and reaction conditions on the MCM-41 formation and its surface area are investigated. The photocatalytic activities of the synthesized MCM-41 and metal loaded MCM-41 are also focused in this study.

To further study and compare the activities of MCM-41 and metal loaded MCM-41s, sellenite bismuth titanate, $Bi_{12}TiO_{20}$, is synthesized due to its piezo-electrical properties and high photocatalytic activity. Thus, it is another interest to study any differences of synthesized sellenite bismuth titanate using titanium glycolate precursor instead of $TiCl_4/TiCl_3$ reported to be very hydrolytically reactive (Umabala $et~al.$, 2000).