CHAPTER I
INTRODUCTION

Titanium dioxide (TiO_2) is widely used in the field of catalysis, as filters or adsorbents or membrane to remove organics from wastewaters (catalytic wet oxidation) and structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts. Transitional metal substituted zeolite frameworks have received considerable attention in recent years due to their catalytic activity in a number of important industrial processes. The titanium doped TS-1 zeolite with the MFI type framework is a well-known catalyst for the selective oxidation of many organic and inorganic compounds with H_2O_2 in mild conditions. The reaction is of interest since water is detrimental to conventional titania-silica catalysts and no environmentally undesirable side products are formed from hydrogen peroxide reactions.

Nowadays, industrial wastewater becomes more and more important problem due to increasing trend of many industries. With the same intention, many researchers have been studying to obtain the efficient wastewater treatment to mineralize all the toxic species present in the wastewater without leaving behind any hazardous residues and with low cost. There are many technologies developed for the wastewater treatment, such as, air stripping, granular activated carbon, biological degradation, chemical oxidation and heterogeneous photocatalysis, having been found to be effective for complete mineralization of many toxic, bacteria and bio-resistant organic compounds in wastewaters at such a milder experimental condition. TiO_2 is one of the famous catalysts for photocatalytic degradation due to its effective activity, chemical stability and non-toxic properties. A practical utilization of photocatalysis process generates the main drawback, involving expensive liquid-solid separation process due to the formation of milky dispersions after mixing the powder catalyst in water

Currently, this drawback has been solved by the use of highly dispersed fine particles in a porous material using TiO_2 membrane. Titania membranes attract a great attention in recent years due to their unique characteristics, such as high water flux, semiconducting properties, photocatalysis and chemical resistances over other membrane materials, such as silica and γ-alumina. Many different types of existing membranes consist of a variety of materials, such as, polymers, metals, mixed solid oxides and porous inorganic materials. However, mixed matrix membrane (MMM), a microencapsulated membrane, becomes more interesting because of its high selectivity combined with an outstanding separation performance of the catalysts, the processing capabilities and low cost of polymers used as matrix.

The important factor to produce titania with good properties is the purity of metal alkoxide precursors. The titanium dioxide has most often been carried out using the titanium alkoxide, however, the synthesis of metal alkoxides is greatly challenging to scientists due to their extreme moisture sensitivity because they contain an unsaturated Ti^{IV} center which is highly reactive to air and moisture therefore the reaction must be carried out under inert gas and another reason is that they used very expensive starting materials

From that worthy knowledge, it brings up an idea to study how to improve the special features, such as, its redox/oxidation properties and its high oxygen mobility. Key point is how to increase specific surface area with homogeneous distribution of pore size. Sol-gel processing has become one of the most successful techniques for preparing nanocrystalline metallic oxide materials. In general, this method involves the hydrolysis and polycondensation of a metal alkoxide, to ultimately yield hydroxide or oxide under well-specified reaction conditions. A gel is defined as a two- or multicomponent system of semisolid nature, rich in liquid and consisting of continuous solid and fluid phases of colloidal dimensions. It contains a stable cross-linked or entangled network structure infiltrated with liquid. The network structure is formed using chemical or physical gelation processes. Chemical gelation produces branched structures based on covalent bonds between the molecules and the network subunits, whereas the physical gelation is determined by forces (Van der Waals, electrostatic, hydrogen bonding) that generate reversible intermolecular associations. The key advantage of preparing metallic oxides by the sol-gel method is the possibility to control their microstructure and homogeneity. Furthermore, the product after sol-gel processing and sintering is easy to be prepared in different forms, such as, powder, monoliths, thin film and membranes. To obtain homogeneous nanoscale macromolecular oxide networks via sol-gel processing, control of hydrolysis is essential. The properties and nature of the product are controlled by the particular alkoxide used, the presence of acidic or basic additives, the solvent and various other processing conditions (e.g. temperature). The calcination temperature is also a key factor, too low a temperature results in incomplete combustion and too high a temperature causes phase transformation.

Although much of the work done to characterize the sol-to-gel transition has used spectroscopic techniques, most of these techniques do not provide information about molecular weights. However, a precise experimental determination of the exact transition point is rather difficult because of its divergent nature. On the other hand, rheological measurements are sensitive to the structural and textural evolution of gels and are complementary to spectroscopic experiments. Oscillatory measurement has received great attention among researchers around the world because of its ability to assess and provide important information on the physical structure and rheological properties of materials without disturbing the material configuration. Knowledge of the evolution in rheological properties during sol-gel processing is a useful guide to the manufacturer when formulating dispersion to optimize the physical properties required in the final product. The shear rheology is an ideal tool for detecting the gel point, using the self-similarity of the structure, which implies that both linear viscoelastic moduli G' and G" follow the same power law with frequency. It is generally accepted that polymeric materials as well as many dispersed particles are viscoelastic. Therefore, the steady shear measurement alone could not fully characterize the rheological behavior of these materials. Consequently, there is a growing need to carry out the rheological dynamic measurement, which can fully characterize both the viscous and the elastic components of the dispersions.

In this work titanium glycolate ($Ti(OCH_2CH_2O)_2$) and titanium triisopropanol amine ($Ti(OCHCH_3CH_2)_2N(CH_2CHCH_3OH))_2$ were synthesized using the Oxide One Pot Synthesis (OOPS) method and low cost starting materials. $Ti(OCH_2CH_2O)_2$ is a novel crystalline complex with infinite one-dimensional chains and exhibits outstanding high stability not only in alcohol but also in water. The high surface area TiO_2 was prepared from the synthesized precursor using the sol-gel process followed by calcinations. The rheological properties of titania and ceria gels were measured at different conditions to study the gelation time and gel strength. The microwave treatment of titanium glycolate and silatrane precursors in basic solution was studied to prepare TS-1 zeolite with high percentage of titanium incorporated in the zeolite framework. The application of titania as a photocatalytic membrane reactor was studied by varying the types of polymer membrane and the amount of titanium loading.