CHAPTER I
INTRODUCTION

1.1 The State-of-the-Art

The excellence in chemical and electronic properties of the ceramics, magnetic, semiconductors and metallic catalysts have attracted a great deal of attention to develop new technologies for the future (Trindade, 2006; Traversa, 1999, 1995; Edelstein, 1998; Koch, 2002). There is an immense interest in implementing sensing devices, in order to improve environment and safety control of gases, which can detect very low concentrations of specific gas pollutants (Traversa, 1999, 1995). There is also a great attempt of this kind of sensors to carry out the optimization of combustion reactions in the merging transport industry as well as domestic and industrial applications (Traversa, 1995). On the other hand, the high activity catalyst with long lifetime is expected for decomposition of huge loading of organic contaminants in waste water from industries. In order to achieve those ultimate goals, the so called "nanoparticles," the diameters of which are in the range of 1-20 nm, have become a major interdisciplinary area of research over the past 10 years (Edelstein, 1998; Koch, 2002).

Nanoparticles have been believed to result in better physical and chemical properties for various applications. They take advantage of high surface area and confinement effects, in which unique properties can be revealed (Edelstein, 1998; Koch, 2002). Thus, particle size is a crucial parameter to control the electronic and chemical properties of materials.

A conventional method that has usually been used to prepare this mixed oxide is precipitation technique. Although the precipitation technique is easy to perform, morphology and size of mixed oxides are difficult to control resulting in unreliable properties for real applications. Among the other techniques, use of microemulsions is one of the most interesting techniques that can be successfully used to control the size of various organic and inorganic materials in their thermodynamically stable microenvironment (Osseo-Asare, 1996; Eastoe, 1996; López-Quintela, 1997, 2003; Mittal, 1998; Capek, 2004).

The previous study on the use of reverse micelle microemulsions of *n*-heptane/water/NaCl/ sodium bis (2-ethylhexyl) sulfosuccinate (AOT) for controlling size, phase and structure of synthesized TiO_2 revealed interesting results (Saiwan, 2004). It was found that the nanostructure of TiO_2 can be controlled with the salinity scan leading to a uniform dispersion and high crystallinity. Moreover, high fraction of anatase phase was obtained. The results also showed an increase in photocatalytic activity to 4-chlorophenol of the synthesized TiO_2 in comparison with commercial TiO_2 (P25). Although the synthesized TiO_2 showed promising properties to enhance photocatalytic activity of TiO_2, further investigation need to be carried out. Therefore, this work will focus on the study of the morphology effect of metal oxides and mixed metal oxides prepared using microemulsions and the role of improving the properties of synthesized metal oxides for real applications such as gas sensors and photocatalyst.

1.2 Objectives

The objectives of this work are:

1. To study the use of microemulsions as nano-reactors for the preparation of single oxides (TiO_2 and SnO_2) and mixed oxides (Nb/TiO_2, Nb/TiO_2-SnO_2).
2. To study the effect of nanostructure and morphology, such as surface area and crystal size of TiO_2, on the photocatalytic degradation of phenol in an aqueous media.
3. To study the use of single and mixed metal oxides as CO gas sensors; the role of nanostructure on gas sensing properties.

1.3 Scope of Works

In this study, the single (TiO_2, SnO_2) and mixed metal oxides (Nb-TiO_2, TiO_2-SnO_2) were synthesized by two microemulsion systems. The first one was the system of anionic surfactant (*n*-heptane/water/NaCl/ sodium bis (2-ethylhexyl) sulfosuccinate (AOT)). The second was nonionic surfactant system of cyclohexane/water/Triton X-100. The applications were divided into two sections, the liquid and gas study. For liquid phase study, the photolysis of organic pollutant (phenol) in aqueous solution by using the synthesized TiO_2 (single oxide system) as a photocatalyst was examined. The morphology effect, i.e. the crystal size, crystal structure, and surface area enhanced adsorption in an aqueous phase, were also studied in details. For gas phase study, both single oxides and mixed metal oxides were synthesized to study the morphology effect on the CO gas sensing properties.

1.4 Metal Oxides and Nanostructured Metal Oxides

Semi-conducting metal oxides have been recognized to have many practical applications, such as in solid state gas sensors or photocatalysts (Edelstein, 1998; Koch, 2002). Among metal oxide materials, TiO_2 and SnO_2 are extremely interesting since they are inexpensive and they have been used in many industrial applications, due to their various properties. TiO_2 has an excellent photocatalytic activity, which can be used to eliminate toxic molecules such as volatile organic compounds in wastewater treatments. Moreover, TiO_2 can be utilized in detection of humidity, methane, and hydrogen gases owing to their electronic properties and high surface area per unit volume. Recently, TiO_2-SnO_2 solid solution in rutile phase has strongly inspired to study the synergism effect of these mixed oxide properties on gas sensoning because of their similarity in electronic properties (Zakrzewska, 2006).

Typically, nanostructured metal oxides show distinct properties from those of the corresponding bulk materials. For example, nanostructured semiconductors exhibit the columbic interaction between electron and hole as well as the shift in energy band gap (Edelstein, 1998; Koch, 2002). In bulk semiconductors (macro-crystalline), the large number of atoms leads to the generation of sets of molecular orbits with very similar energies, which effectively from a continuum. At 0 K, the valence band is filled with electrons, while the conduction band consisting of the higher energy levels is unoccupied. The two bands are separated by an energy band gap (Eg), which typically is in 0.3-3.8 eV range. Above 0 K, the electrons in the valence band may receive enough thermal energy to excite across the band gap into the conduction band, resulting in holes in the valence band forming "electron-hole pairs". Therefore, the conductivity (σ) is governed mainly by the number of electron-hole pairs, charged carried concentration (n) and their mobility (μ). For nanostructured semiconductors, the electrons and holes are closer together than in the macro-crystalline materials. Accordingly, the columbic interaction between electron and hole and the shift in energy band gap cannot be neglected with respect to those of typical macro-crystalline semiconducting oxides.

1.4.1 Photocatalytic Degradation

Photocatalysis is a well known reaction of TiO_2 for the degradation of organic pollutants such as phenol in the environment, which has been found to be a technique with high potential for industrial waste water treatment (Alemany, 1997; Ilisz, 1999; Peirò, 2001; Subramanian, 2001; Serpone, 2002). It has been suggested that the mechanism of phenol decomposition follow four main steps. The first step is a charge separation (electron hole pair) of nonocrystalline TiO_2 under UV illumination (reaction 2.1). Then, the hole is reacted with adsorbed water to form $^{\cdot}OH$ radicals (reaction 2.2). The next step is the reaction of $^{\cdot}OH$ radicals with phenol to form intermediate products, and finally to form CO_2 and H_2O (reaction 2.3). The last step (reaction 2.4) is the recombination of electron and hole, which is believed to control the rate of decomposition due to the long-lasting life of electrons. The recombination step also depends on the energy band gap of TiO_2. The nanocrystalline TiO_2 presents a higher energy band gap ($\geq$ 3.23) than the macrocrystalline TiO_2. Nanostructured TiO_2 is expected to slowdown the rate of recombination (reaction 2.3) due to an increase in electron band gap (more than 3.2 eV) due to confined space in the nanostructure.

Other important effects that play an important role in the photocatalytic degradation is catalyst morphology, such as phases, surface area, crystal size, and shape. Thus, the application of nanostructured TiO_2 takes advantages of high surface area and confinement effect which lead to different properties from those of conventional materials. Although there are many works that have studied photocatalysis using nonocrystalline TiO_2, only the effect of phase composition is normally focused on (Alemany, 1997; Ilisz, 1999). There are few works that showed the effect of various sizes of nanocrystalline powder on the rate of photocatalysis.

$$TiO_2 \xrightarrow{hv} TiO_2\,(e + h) \qquad (2.1)$$

$$TiO_2\,(e + h) + OH^- \longrightarrow TiO_2\,(e) + {}^*OH \qquad (2.2)$$

$$TiO_2\,(e + h) \longrightarrow TiO_2 \qquad (2.3)$$

$$O_2 + e \longrightarrow O_2^- \qquad (2.4)$$

1.4.2 Gas Sensors

Depending on the technology applied in the developments stages, gas sensor devices can be divided in three big groups: solid state, spectroscopic and optic. While the spectroscopic and optic systems are very expensive and present sometimes difficulties to implement in small spaces, the solid-state sensors posses great advantages, due to their fast sensing response, simple implementation and low cost (Takeuchi, 1998; Cirera, 2000; Barsan, 2001). Solid-state gas sensors are based on changes of physical and/or chemical properties of their sensing materials when exposed to different gas atmospheres. The changes in conductivity of the sensing materials in the presence of specific gas are verified [Fig. 2.1].

The conduction is determined by the effect of surface and bulk conductance. The basic mechanism utilizes the presence of Schottky barriers at the grain boundaries (back-to-back Scottky barrier) in loose contacting grains and surface layer overlapping at the neck of n-type semiconducting oxide. When the oxygen from ambient adsorbs on the exposed surface of the grain, the electrons from oxide are extracted and ionized to O^- or O^{2-} leading to the depletion region, or Debye length (L_D) formation. The conduction is determined by the height of the barrier ($E_S = qVs$) at the intergranular contacts;

$$\sigma_S=\sigma_O\exp(-qVs/kT) \qquad (2.5)$$

where σ_S and σ_O are the conductivity and pre-exponential constant, respectively: when exposed to a reducing gas such as CO, the adsorbed CO can react with the adsorbed O^-, releasing the trapped electrons back to the conduction band, and subsequently lowering the barrier height and resistance.

TiO_2 and SnO_2 are the semiconducting oxides mostly used for commercial gas sensors of this kind. Sensitivity, selectivity and stability are key properties to improve gas sensing of these materials (Shimizu, 1999; Cirera, 2000).

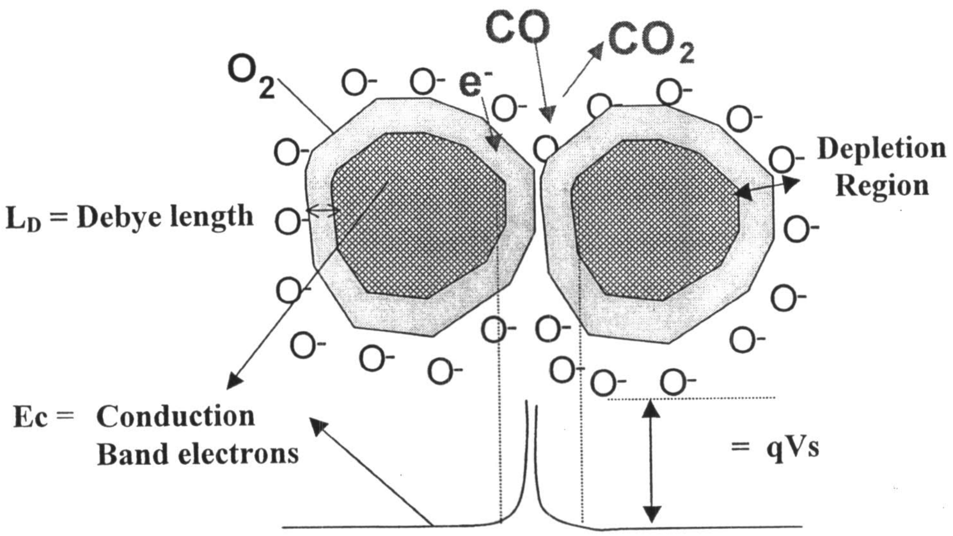
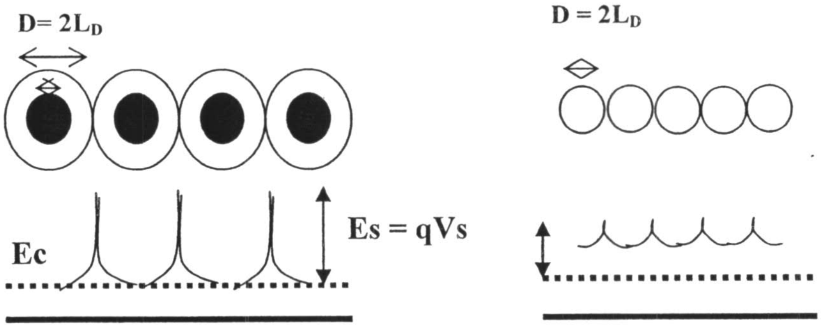


Figure 1.1 Change in resistance of semiconducting materials.

Nanostructured metal oxides have a strong impact on physical properties of semiconductor sensors leading to a significant increase in sensitivity. The grain size or crystallite size (D) and the space-charge depth (L_D) are critical for the response to the gas contaminant (Shimizu, 1999). Figure 2.2 show the effect of grain size on the conduction through the grain of semiconductors. For $D \geq 2L_D$, the metal oxide resistance is directly related to the barrier (Es; grain-boundary control). On the other hand, if $D \leq 2 L_D$, the grain resistance dominates the resistance of the whole chain and, in turn, the sensitivity is controlled by grain themselves (grain control). Accordingly, the sensitivity of the metals oxide is suddenly increased. The $2L_D$ of TiO_2 and SnO_2 are 4 and 3 nm, respectively. It has been reported that the sensitivity of SnO_2 increases five times when the size of nanostructured SnO_2 is reduced from 8 to 5 nm, which is very closed to $2L_D$ of SnO_2 (Shimizu, 1999).



(a) $D \geq 2L_D$ (b) $D \leq 2L_D$

Figure 1.2 Change in conduction through nanostructured metal oxides.

Beside that, typically the nanostructured materials will be highly selective to gases, taking into account that sensing reactions occur at the surface. A small increase in gas adsorption on the oxide surface can cause a significant change in the electrical resistance of the material. Thus, the control of surface will be one of the first requirements for enhancing the sensitivity of a sensor (Shimizu, 1999). On the other hands, the selectivity can be improve by introducing catalytic additive for enhancing activity toward the target gas and reduce the rest. The stability, which is the repeability of device after long time use can improve by introduce dopants or pretreated the materials. Nanostructure of metal oxides with dopants also creates the selective surface structure and electronic properties of oxide particles. This is probably enhanced the gas adsorption for sensor applications.

1.5 Microemulsions

Microemulsions are defined as transparent dispersions containing two immiscible liquids with particles of 1-100 nm in diameter obtained upon mixing two immiscible liquids. Microemulsions may be water-external (o/w) or oil-external (w/o), or both. They can be generally prepared with more than one surfactant or with a mixture of surfactants and cosurfactants with the appropriate combination.

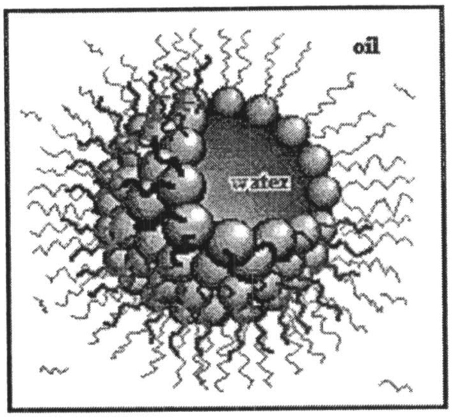


Figure 1.3 Reverse micelles microemulsion (w/o).

Reverse micelles microemulsion (w/o) are of specific interest in this study because a variety of reactants can be introduced in the reverse micelles core (Figure 2.3). A huge number of micelles core in nano-sized diameter dispersed on the continuous (oil phase) can be used as uniform micro reactors to confine and control the size and shape of many organic or inorganic materials, such as polymer, GeO_2, In, Pd, Pt, Fe and Silica (Giordano, 1995; Eastoe, 1996; Raman, 1996; Qi, 1997; Debuige, 2000; Kaneko, 2000; Wang, 2000, 2001; Escudero, 2002; Kuang, 2002; Guo, 2003; Xu, 2003; Huang, 2004).

Typically, the shape and size of the dispersed nanodroplets are mainly governed by the curvature free energy and are determined by the elastic constant and the curvatures of the surfactant film. The elasticity of the film depends not only on the surfactant type and the thermodynamic conditions, but also on the presence of additives, like alcohols, electrolytes, block copolymers, and polyelectrolytes. In the past, mainly spherical (and in some cases elongated) nanodroplets have been prepared.

1.6 Nanostructured Metal Oxides Synthesized using Microemulsions

Many researchers have been focused on methods to improve the properties of metal oxides, such as TiO_2 and SnO_2, using microemulsions (Chabra, 1995; Lim, 1996; Martinelli, 1998; Kim, 1999, 2001; Li, 1999; Song, 1999; Stathatos, 1999; Mori, 2001; Jadhav, 2003). The high surface area in nano-level size is the key factor to control the size of reverse micelles (Chabra, 1995; Kim, 1999, 2001; Li, 1999; Stathatos, 1999; Mori, 2001; Jadhav, 2003). However, those works have been investigated the synthesis of single oxides (binary systems) such as TiO_2, SnO_2 and In_2O_3. However, mixed metal oxides can expand the fields of application are still specific of oxides. For example, TiO_2 can be used as a gas sensor being anatase the most sensitive phase. However, at the temperature needed for application of sensor in exhaust gas pollution monitoring in the automobiles, anatase phase is not stable and can transformed into rutile, less sensitive structure. In this case, the single oxide alone can not be used. Thus, mixed metal oxides are better for various applications. For example, Nb, Ta, Ga and Cr can be used as dopants into nanostructured TiO_2 to increase its thermal stability to allow the use for exhaust gas pollutant monitoring (Carotta, 1999; Bonini, 2000; Ferroni, 2000; Shi, 2000; Traversa, 2000, 2001; Zakrzewska, 2004).

Typically, the work on synthesis of mixed metal oxides has been focused on sol-gel or precipitation techniques, i. e., the synthesis of SnO_2-TiO_2, $BaZrO_3$, $SrTiO_3$ (Herrig, 1996; Sharma 2001). Very limited research works are focused on the mixed metal oxides synthesis using microemulsion techniques. Therefore, the aim of this work is focused on the preparation of a variety of metal salt mixed in the reverse micelles core of microemulsions for mixed metal oxide synthesis.