CHAPTER II
LITERATURE SURVEY

2.1 Silver Catalyst and Oxygen Adsorption Mechanism

Silver is known for its unique catalytic properties in gaseous phase oxidation reactions, particularly ethylene oxidation reaction. The effect of silver particle size on the reaction rate is in the opposite direction to other catalysts. The catalytic properties of silver change sharply for particles that are abnormally large (hundreds of °A) a surprising result since the properties of such abnormally large particles should not differ from those of the bulk (Goncharova et al., 1995). Numerous authors observed a catalytic size effect of silver within the 100-1000 °A range and explained it by the changes in the surface structure, particle morphology and support effect (Harriot, 1971). The influence of these factors as well as a broad particle size distribution result in a wide range of crystal sizes for crystal sizes for which the changes in catalytic activity can be particularly sharp. Lee et al. (1989) studied supported silver catalysts and found a three-fold increase in the reaction rate with increasing silver particle sizes within 150-400 °A. This was explained by a decrease of the the proportion of small particles (< 100 °A). These small particles are known to exhibit no catalytic activity. As a rule, this was assumed to relate to the over oxidation of small Ag particles to inactive Ag_2O. Some studies provided the useful finding that Ag particles, in particular the small ones, can migrate over the supporting surface.

Lee et al. (1989) concluded that the specific activity of silver could vary by as much as a factor of 50 depending on the support employed. Moreover, the influence of metal crystallite size was also found to depend on the carrier employed. They also showed that the low or zero apparent selectivity of silver supported on various carriers was primarily due to isomerization and oxidation of ethylene oxide on sites supplied by the support material. All conventional and non-conventional carriers examined exhibited activity towards ethylene oxide isomerization and combusion, with exception of α-alumina.

Cheng and Clearfield (1985) used zirconium phosphate which is a non-conventional support material and observed a decrease in activity of the catalyst when the surface area of the support was increased.

Commercial silver catalysts, commonly, consist of 10-15 wt.% silver on low surface area α-alumina. High metal content is necessary to provide a large active surface area, albeit with a very low degree of dispersion. However, if a higher degree of dispersion of the metal could be achieved, the same active area could be obtained with significantly smaller amount of silver. As a consequence of this, the precious metal could be utilized more efficiently and the process would become more economical. A high degree of metal dispersion can usually be achieved by employing high surface area supports (Bulushev et al., 1995).

Ishii et al. (1992) studied a method for the treatment of waste water. This method was wet oxidation with a molecular oxygen-containing gas of an amount 1.0 to 1.5 times the amount of theoretically necessary for decomposing the organic substances in the waste water to nitrogen, carbon dioxide, and water at a temperature not exceeding 370 °C under a pressure enough for this waste water to retain a liquid phase in the presence of a solid catalyst comprising of a first catalytic component formed of titanium dioxide, a second catalytic component formed of the oxide of an element of lanthanide series, and a third catalytic component containing at least one metal selected from the group consisting of manganese, iron, cobalt, nickel, tungsten, copper, silver, gold, platinum, palladium, rhodium, ruthenium and iridium. The catalyst is sparingly decomposable under the conditions of wet oxidation and is, therefore, capable of exhibiting a high catalytic activity to acetic acid which often persists in a high concentration in the waste water during the treatment.

Heinig (1994) proposed an effective new method of treating water against micro-organisms including bacteria without the use of significant amounts of chlorine or other objectionable chemicals. More specifically, The effective method of treating water was performed by generating an active oxidizer in the water which is capable of attacking and killing a wide range of micro-organisms. A relatively inert material, such as PVC, was used rather than activated charcoal. The silver catalyst utilized in the method comprised an alumina matrix having between approximately 0.1% and 5% by weight of elemental silver chemically deposited. It was found that this method could be effectively utilized for treating water in order to kill various micro-organisms contained. The water was immediately rendered safe for human consumption and/or for use in pools, spas, etc. It was further found that when a low and unobjectionable level of a salt of the type specified was added to water prior to the treatment thereof by the method, the salt was converted to safe and effective active oxidizer which was relatively stable under most conditions so that it had a prolonged beneficial effect with respect to maintaining the bacteria level in the treated water at a safe level.

One of the most important roles of silver catalyst towards ethylene oxidation reaction is its mechanism of oxygen adsorption. The oxygen complexes adsorbed on silver have been characterized by a wide variety of studies, including calorimetric studies, infrared spectroscopy, isotopic exchange, electron diffraction, and kinetic studies of adsorption rates (Satterfield, 1991). A reaction mechanism which was considerably advanced was proposed by Kilty and Sachtler (1974) and was also discussed by Carra and Forzatti (1977). It was proposed that diatomic oxygen be adsorbed onto a single silver atom. This molecular oxygen may be somewhat ionic or so called oxygen super-ion or superoxide free radical(O_2^-). The mechanism can be written as:

$$O_2 + Ag \text{ -------->} O^-_{2\,(ads)} + Ag^+$$

The ability of silver deposited on alumina in generating oxygen super-ions for water sterilization is in focus. We, basically, believe that this active oxygen can react with organic materials, including bacteria, and shows its oxidizing power on killing bacteria suspended in drinking water. For example, oxygen super-ions can oxidize cystein in polypeptide to change in its configuration and activity so metabolic activity can be inhibited.

2.2 Supports

The concept of a support is an inert substance that provides a means of spreading out an catalyst ingredient or a means of improving the mechanical strength of weak catalyst. Moreover, it can also enhance and stabilize the catalytically active structure. The support may be used as pellets or powder. The selection of a support is based on its having certain desirable characteristics. In addition to possible chemical effects, certain physical properties are important. There are inertness to undesired reactions, stability under reaction and regeneration conditions, desirable mechanical properties, surface area, porosity including average pore size and pore size distribution, and low cost (Satterfield, 1993).

In this study, alumina was chosen as a support. Alumina is the most widely used industrial support because it is inexpensive and structurally stable. It can also be prepared with a wide variety of pore sizes and pore size distributions. Commercial materials are available with surface areas in the range of 100 to 600 m^2/g and down to essentially nonporous alumina.

2.3 Pathogens and Pathogen Indicators

The bacteria found in water are simple categorized into three types: natural aquatic bacteria, soil dwelling organism, and organisms that normally inhabit the intestines of human and other animals. From the perspective of human use and consumption, the most importance of biological organisms in water are pathogens, those organisms capable of infecting or of transmitting diseases to human. Analysis of water for all pathogens would be very time-consuming and extremely difficult to cultivate in laboratory. Tests of specific pathogens are usually made only when there is a reason to suspect that those particular organisms are present. Normally, the purity of water is checked using indicator organisms (Peavy et al., 1985).

For the purpose of determining the portability of a water supply, it is necessary to establish that the water is not contaminated with pathogenic micro-organisms. Since intestinal pathogens, if present, would be greatly out numbered by normal intestinal inhabitants such as *Escherichia coli*, it is more satisfactory to examine the water for the presence of the latter organisms, which, if found indicate that pathogens could be present.

Escherichia coli, E.coli, is a good indicator organism. The presence of this bacterium in water indicates that recent fecal pollution has occurred (Peavy et al., 1985). Moreover, *E. coli* bacteria is widely studied and it is safer to handle than all pathogens.

2.4 Concept on Testing of Microorganisms

There are several methods used for testing bacteria in water such as most probable number or MPN technique, membrane filtration technique and plate count method. The membrane filtration technique is a method that is highly reproducible and is extremely useful in monitoring drinking water and a variety of natural waters. One advantage of membrane filtration is that a small number of organisms can be detected since the amount of water passed through the membrane is restricted only by the amount of gross suspended matter present in the water. Another advantage is that the counts can be carried out in a relatively short time. From statistical comparisons of results obtained by MPN technique show that the membrane filtration technique is more precise (APHA, 1985). In the test, a portion of sample is filtered through a membrane. The membrane pores do not exceed 0.45 microns. Bacteria are mostly retained on the filter which is then placed on selective media to promote growth of coliform bacteria while inhibiting growth of other species. The membrane with media is then incubated at the appropriate temperature for the appropriate period of time, allowing bacteria to grow into visible colonies that are finally counted.