

## **CHAPTER II**

### **BACKGROUND AND LITERATURE SURVEY**

Several techniques for natural gas dehydration are described in details here. Then the focus will be shifted to the dehydration using solid adsorbent. Review of applications of alumina in the adsorption separation process will be followed. Next, details on the sol-gel technology will be summarized. Finally, works related to solid adsorbents prepared by the sol-gel techniques will be discussed.

#### **2.1 Background**

##### 2.1.1 Dehydration in Natural Gas Process

Natural gas and associated condensate are usually produced from gas reservoirs that are saturated with water. In addition, the gas and the condensate often contain impurities, such as water and mercury, which must be eliminated. Although water vapor itself is not as harmful as mercury, it is still necessary to remove water content from the gas process. Whether in gathering systems or transmission pipelines, it is possible that the water content may reach its condensation temperature and hydrated components can be formed. Transportation of wet gas through pipelines and others equipment can result in pipeline plugging. Even in areas where pipeline temperature does not reach the hydrate range, temperature variations may lead to water condensation with consequently loss of pipeline capacity and efficiency (Campbell, 1992).

A dehydration process has been applied as a way to remove water in the natural gas stream. The major purposes of this process are to prevent formation of hydrates and condensation of water along processing and

transportation facilities, to satisfy the water content specification, and to prevent corrosion problems.

There are several technologies for natural gas dehydration (Campbell, 1992):

- adsorption using liquid adsorbents
- adsorption using solid adsorbents
- dehydration by refrigeration
- dehydration by membrane permeation, and
- dehydration by gas stripping

Because of special maintenance required, high capital cost, and the limited specification of the gaseous components to be used, the dehydration by refrigeration has not been widely used as much as other methods (Campbell, 1992). For the membrane permeation, several attempts have still been done to develop the most effective membrane with lower expense to meet the industrial needs. Both liquid and solid adsorbents are the most favorable choices. Liquid adsorbent dehydration equipment can easily be automated for unattended operation but additional precautions in the system design are needed due to the solubility of those gases, especially acid gas, in the adsorbent solution (Campbell, 1992).

Solid adsorbent dehydration has been proven to be the first alternative for water vapor removal design. Adsorption column, packed with a suitable hydrophilic adsorbent, which is used as a drier for the removal of traces of moisture from the gas stream, is the basic scheme of this separation system. Without any solubility problem, various choices of adsorbent to be used and ease in regeneration are a few advantages of this technique. For such gas mixtures, it is generally possible to find an adsorbent for which the adsorption separation factor is much greater than the relative volatility so that a more economic adsorptive separation is in principle possible (Ruthven, 1984). However, for an adsorption process to be developed on a commercial

scale, it requires the availability of a suitable adsorbent in tonnage quantities at economic cost. This has stimulated fundamental research in adsorption and led to the development of new adsorbents.

### 2.1.2 Solid Adsorbents for Dehydration Process

Many types of solid adsorbents, which possess physical characteristics to adsorb water from natural gas, can be found in adsorbent catalogues, these days. These adsorbents generally are used in the dehydration systems consisting of two or more towers and associated with regeneration equipment. The requirement for adequate adsorptive capacity restricts the choice of adsorbents for practical separation process to microporous adsorbents with pore diameters ranging from a few angstroms to a few tens of angstroms.

To choose a solid adsorbent for using in any adsorption process, several requirements need to be considered. Normally, the selection of an adsorbent is based on its characteristics. In addition to possible chemical effects, certain physical properties are important. The major properties of an adsorbent needed to consider in such case include its inertness to undesired reactions, hardness and resistance to compressive strength, stability under reaction and regeneration conditions, surface area (high surface area is usually, but not always, desirable), pore size distribution and low investment cost.

The search for a suitable adsorbent is generally the first step in the development of an adsorption separation process. Since the separation factor generally varies with temperature and often also with composition (Ruthven, 1984), the suitable condition to maximize the separation factor is a major consideration in process design.

The commercial solid adsorbents, which can be used for water dehydration, can be divided into three major types:

Alumina - an iron free synthetic *bauxite* (naturally mineral composed of primarily of  $\text{Al}_2\text{O}_3$ ), which is activated by heating.

Silica Gels - a granular, amorphous solid composed largely of  $\text{SiO}_2$ ; manufactured and conditioned by chemical reaction to have an affinity for water.

Molecular Sieve - an manufactured or naturally occurring aluminosilicates exhibiting a degree of selectivity based on their crystalline structure.

Alumina is a porous high surface area form of aluminum oxide, prepared either directly from bauxite ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) or from the monohydrate by dehydration and recrystallization at high temperature. The surface is more strongly polar than that of silica gel and has both acidic and basic character, reflecting the amphoteric nature of the metal (Ruthven, 1984). It is used for gas and liquid dehydration and will give outlet dew points in the range of  $-37.8^\circ\text{C}$ . Less heat is required to regenerate alumina than molecular sieve, and the regeneration temperature for alumina is lower than that of silica gel (Bailon *et al.*, 1999).

Silica gel is the generic name for a gel manufactured from sulfuric acid and sodium silicate. The chemical composition can be expressed as  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ . The water content, which is present mainly in the form of chemically bound hydroxyl groups, amounts typically to about 5% wt. The material appears first to have been developed during the First World War for use in gas masks (Ruthven, 1984). It is used for gas and liquid dehydration and hydrocarbon recovery from natural gas stream. When used for hydrocarbon removal, the units are usually called HRU's (Hydrocarbon Recovery Units) or SCU's (Short Cycle Units). When used for dehydration, silica gel will give outlet dew points of approximately  $-21.1$  to  $-26.7^\circ\text{C}$ .

Molecular sieves are a class of aluminosilicates and possess the highest water adsorption capacity. They will produce the lowest water dew

points, and can be used to simultaneously dry gases and liquids. Their equilibrium water capacity is much less dependent on adsorption temperature and relative humidity (Satterfield, 1991). They also are usually rather expensive.

### 2.1.3 Activated Alumina

Activated aluminas comprise series of nonequilibrium forms of the partially hydroxylated aluminum oxide,  $\text{Al}_2\text{O}_3$ . The chemical composition can be represented by  $\text{Al}_2\text{O}_{(3-x)}(\text{OH})_{2x}$  where  $x$  ranges from 0 to 0.8. It is a porous solid made by the thermal treatment of aluminum hydroxide precursors and finds applications mainly as adsorbent, catalyst, and catalyst support (Perason and Grant, 1992). The term “activation” is used to indicate a change in its properties resulted from heating (calcination). Other names for these products are active alumina, gamma alumina, and catalytic alumina.

In general, the surface of activated alumina is a complex mixture of aluminum, oxygen, and hydroxyl ions combine in specific ways to produce both acidic and basic sites. These sites are the cause of surface activity and are important in adsorption, chromatographic, and catalytic applications.

#### Preparation

The majority of activated alumina products are derived from the activation of aluminum hydroxide, rehydrated alumina, or pseudoboehmite gel. Other commercial methods to produce the specialty activated alumina are the roasting of aluminum chloride,  $\text{AlCl}_3$ , and the calcination of precursors such as ammonium alum,  $\text{AlH}_7\text{NO}_8\text{S}_2$ . Processing is tailored to optimize one or more of the product properties such as surface area, purity, pore size distribution, particle size, shape, or strength.

#### *Activated Aluminum Hydroxide*

The main precursor for this preparation technique is gibbsite derived from the Bayer process (Perason and Grant, 1992). The Bayer process

gibbsite is available in large quantities as an intermediate product in the aluminum production. Low cost, relative high purity, and availability make gibbsite a raw material of choice for many activated alumina products.

#### *Rehydration Bonded Alumina*

The rehydration bonded aluminas are agglomerates of activated alumina, which derive their strength from the rehydration bonding mechanism. Since several steps are involved in the manufacture, they are generally more expensive than the activated alumina hydroxides. On the other hands, the rehydration bonded alumina can be synthesized in a wider range of particle shape, surface area, and pore size distribution (Perason and Grant, 1992).

#### *Gel-Based Activated Alumina*

The alumina gels can be formed by the wet chemical reaction of soluble aluminum compounds. An example is the rapid mixing of aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{XH}_2\text{O}$ , and sodium aluminate,  $\text{NaAlO}_2$ , solution. After extensive washing to remove the sodium sulfate, the resulting gel can be dried or partially dewatered and formed directly by extrusion or oil drop. If the gel is dried prior to forming, it can be ground to fine particle size, then mixed with water and tumbled or formed by the general processes. The materials are then activated to produce relatively pure phase gamma alumina. The gels made from aluminates and aluminum salts must be carefully washed to remove undesirable anions and cations (Perason and Grant, 1992).

### Applications

#### *Catalytic Application*

The activated alumina is used commercially in catalytic processes as a catalyst, catalyst support, or as a modifying additive. The activated alumina serves as the catalyst in the Claus process for recovering sulfur from  $\text{H}_2\text{S}$  that originates from natural gas processing or petroleum refinery operations. The alumina is generally in the form of spheres, about 5 mm in diameter. This size has evolved as a good compromise between high

activity and low pressure drop of alkali, which has been claimed to enhance performance in Clause reaction (Perason and Grant, 1992).

#### *Chromatographic Application*

The activated alumina has been used for many years in the separation of various organic compounds by the normal phase chromatography because of its natural hydrophilic surface characteristics. More recently, the stable surface coatings have been developed which impart hydrophobic properties to the particle surface. These coatings, coupled with the improved technology to produce closely sized particles have allowed alumina to compete in reverse-phase packing material. Alumina has better chemical stability at the moderately high pH levels, which gives it a natural advantage for separation in this pH range (Perason and Grant, 1992).

#### *Membranes*

The membranes comprised of activated alumina films less than 20  $\mu\text{m}$  thick have been reported. These films are initially deposited via the sol-gel technology from the pseudoboehemite sols and are subsequently calcined to produce controlled pore size in the 2 to 10 nm ranges. The inorganic membrane systems based on this type of film and supported on the solid porous substrates have been introduced commercially. It was claimed to have better mechanical and thermal stability than the organic membranes. The activated alumina film comprises only a miniscule part of the total system.

#### *Adsorbent Application*

One of the earliest uses for activated alumina was the removal of water vapor from gases and this still remains an important application. Under equilibrium conditions, alumina adsorbs an increasing amount of water as the relative humidity of the contacting gas increases. By heating the activated alumina to about 252°C under low relative humidity conditions, essentially all of the adsorbed water is removed and the alumina can return to its original

state. This adsorption-regeneration cycle can be repeated hundreds of times with little deterioration of the adsorbent properties (Perason and Grant, 1992).

#### 2.1.4 Alumina Applications in Adsorption

Alumina has been used as an adsorbent for many decades because it is inexpensive, structurally stable and can be prepared with a wide variety of pore size and pore size distribution. The earliest known use of alumina was in the chromatographic separation of liver extract by Folkers and Shovel (1901). In the 1930s when the laboratory-scale chromatography became a common analytical technique, aluminas were the packing material of choice.

At the beginning of 1940s, the application of alumina was shifted to be an adsorbent. Both air and natural gas dehydration were being routinely performed with waste heat regeneration of alumina columns (Goodboy and Fleming, 1984). Aluminas were applied in the 50s and 60s to the isotropic separation of many actinide series compounds and some specialty organics. In 1960s, alumina was also used in the impurity separation process of halogenated compounds from the aqueous streams and the organic acids from hydrocarbons. Degenerative of carboxylic acid from lubricating oils is an example (Goodboy and Fleming, 1984).

Environmental concerns have also established new applications for alumina in the gas treatment. Although not of the magnitude of activated carbon air purification, adsorption of acid gases and sulfur species in petroleum-related industries constituted a significant portion of adsorbent alumina utilization in the 1970s. These areas have received even greater attention in the 80s (Goodboy and Fleming, 1984).

Because the chemical functional groups that can be adsorbed on alumina are so diverse, the modification of alumina surface is becoming popular. These involve the chemical treatment of the alumina surface to



introduce new functionality which can enhance adsorption. A good example is the modified alumina used for the separation of mercury from natural gas streams in the Arab oil countries (Goodboy and Fleming, 1984).

Additional field, in which the alumina adsorption technology has made inroads recently, is biological processing. Because of the ability to modify surface characteristics, define pore structure, and exhibit good physical and chemical stability with consistency, aluminas are finding successful application in commercial processing of biological materials (Goodboy and Fleming, 1984).

As successful large-scale chromatographic technology continue to be demonstrated, the trend toward use of aluminas in greater numbers of bulk, as well as impurity separation, is expected to increase. The simulated moving bed process developed by UOP, the Oak Ridge annular rotating multiple extraction system, as well as other designs for the continuous chromatography will provide additional options in commercial separations other than those exist today.

## **2.2 Adsorbent Preparation**

### **2.2.1 Sol-gel**

The sol-gel technique is a method to produce solid from gel. This preparation method starts with a metal alkoxide. The alkoxide in an organic medium is first hydrolyzed by addition of water, followed by polymerization of the hydrolyzed alkoxides through condensation of the hydroxyl groups. When the extent of polymerization and cross-linking of polymeric molecules become extensive, the entire solution becomes rigid and a solid gel is formed (Kung and Ko, 1996). Gel can also be formed from stabilized sols. Often sols are stabilized colloidal aggregates of small metal oxyhydroxy particles in an aqueous medium. These aggregates can be broken

up by peptizing agents. Controlling the hydrolysis and condensation between particles lead to aggregation and the formation of gel in a three-dimensional network of particles in a polymeric matrix. With an alkoxide ( $M(OR)_n$ ) as a precursor, sol-gel chemistry can be described in terms of two separated reactions (Ward and Ko, 1995),



During the initial reaction, usually referred to as “pregelation” step (Gonzalez *et al.*, 1997), the reactants hydrolyze and condense to form gel. The hydrolysis occurs when water is added to the alkoxide, which is usually dissolved in alcohol. Intermediates obtained as a result of this reaction include oligomers of the acid, which correspond to the alkoxide used, and ether oligomers, which are finally transformed into gel and contain large amounts of water in their structures. In addition to those oligomers, a nonhomogeneous crystalline microstructure encapsulated within the initial amorphous solid is also formed. In the condensation or polymerization reactions, aldoxi groups ( $-MOR$ ) react with hydroxyl groups ( $-MOH$ ), which was formed during the hydrolysis step, to form metaloxanes ( $-MOM-$ ). During this step the primary structure and the properties of the gel are determined. These reactions occur simultaneously and usually do not go to completion. It is important to note that the conditions, under which the condensation reaction occurs, are important in determining the nature of the final product as either a gel or a precipitate.

Any factors that affect either or both the hydrolysis or the condensation step are likely to impact properties of the gel. Parameters that

affect the structure of the initial gel, and, in turn, the properties of the finished substance are type of precursor, type of solvent, water content, acid or base content, precursor concentration, and temperature (Ward and Ko, 1995). In addition, solid prepared by the sol-gel technique achieves very high purity because of quality of the available precursor. Furthermore, textural properties of the product, most notably surface area and pore size distribution, can be tailored.

Handy *et al.* (1991) found that because of different extent of polymeric chain branching, acid-catalyzed gels contained mostly micropores whereas base-catalyzed ones contain mesopores. Ying and Benziger (1993) recently showed that acid-catalyzed gels contain higher concentration of adsorbed water, silinol groups, and unreacted alkoxy groups than base-catalyzed ones.

Fahrenholtz *et al.* (1992) prepared a series of base-catalyzed silica gels by using a mixing precursor of tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTEOS). The authors found that when the mole fraction of MTEOS exceeded about 0.50, there was a significant change in the physical morphology of the gel that translated into a large decrease in surface area and pore volume of dried sample.

The second stage in the sol-gel synthesis is referred to as the “postgelation” step (Gonzalez *et al.*, 1997). Changes, which occur during the drying and calcination of the gel, include the desorption of water, the evaporation of the solvent, the desorption of organic residues, dehydroxylation reactions and structural changes. The evaporation of the solvent during drying leads to the formation of strong capillary forces. These capillary forces arise from differences between solid-vapor and solid-liquid interfacial energies. The huge interfacial area of the gel (300-1,000 m<sup>2</sup>/g) can result in capillary pressure as large as 100 MPa. Because it is possible to develop large pressure gradients within the gel structure, the network is compressed to a greater

extent at the exterior surface. This differential strain results in cracking. Solvent removal under supercritical drying conditions (243°C) and 63 atm for ethanol results in the elimination of the liquid-vapor interface and a preservation of the gel microstructure.

Several advantages of the sol-gel technology were reported by Ward and Ko (1995). With this technique, it is possible to control composition and structure at a molecular level, to introduce several components in a single step, to impose kinetic constraints on a system and, thereby, stabilize metastable phases. Other advantages include superior homogeneity and purity of material, better microstructure control of metallic particles, higher BET surface area, improved thermal stability of the material, and well-defined pore size distributions.

At this moment, the flexibility of ways to make a sol-gel sample has enabled researchers to gain insight into fundamental aspects. The ability to control factors offers by sol-gel preparation adds another experimental specific hypothesis. This level of understanding is crucial to the design and preparation of better catalytic material.