

**OPTIMIZATION OF NATURAL GAS PURIFICATION FROM SULFUR IMPURITIES USING MODIFIED CLINOPTILOLITE ADSORBENTS**

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**Abstract**

This paper investigates the enhancement of the adsorption properties of natural clinoptilolite for the purification of natural gas from harmful sulfur-containing components, specifically hydrogen sulfide (H<sub>2</sub>S) and organic sulfur compounds (mercaptans, COS). The study focuses on the acid modification process (dealumination) to optimize the pore structure and increase the dynamic capacity of the adsorbent. Experimental results demonstrate that modified clinoptilolite exhibits significant efficiency, comparable to synthetic zeolites, while offering substantial economic and environmental advantages. The industrial feasibility of the proposed sorbent was validated through pilot tests.

**Keywords**

Natural gas, Clinoptilolite, Adsorption, Sulfur compounds, Acid modification, Dealumination, Zeolites.

**1. INTRODUCTION**

The increasing global demand for clean energy has made the efficient processing of natural gas a critical industrial priority. Many natural gas deposits contain significant concentrations of sour components, primarily H<sub>2</sub>S, CO<sub>2</sub>, and various mercaptans. These impurities are not only toxic and corrosive to pipeline infrastructure but also act as catalytic poisons in downstream chemical synthesis.

Traditional gas purification relies heavily on synthetic zeolites (e.g., NaX, CaA). However, their high production costs and sensitivity to acidic environments limit their economic efficiency. Natural zeolites, particularly clinoptilolite, represent a cost-effective alternative due to their high thermal stability and abundance. This research addresses the limitation of natural clinoptilolite—its narrow pore diameter—by applying chemical modification techniques to broaden its applicability in deep gas desulfurization.

**1. Industrial Applications of Zeolites (Introduction Section)**

Zeolites play a crucial role in various industrial processes, particularly in the purification and dehydration of diverse gas streams. Their primary functions include:

- Dehydration and purification of gas mixtures with varying compositions.
- Separation of hydrocarbon gases based on their molecular sieve properties.
- Utilization of specific adsorbents such as 5A (CaA), X, Y, and mordenite for removing acidic oxides, specifically SO<sub>2</sub> and H<sub>2</sub>S, from gas streams.

**Classification of Sulfur Removal Processes**

Currently, more than 20 processes are used in the industry to treat gases containing sulfur compounds. These processes are categorized into two primary groups:

**Group I:** Designed for the removal of hydrogen sulfide (H<sub>2</sub>S) only. The chemical mechanism is based on the acidic properties of H<sub>2</sub>S, utilizing weak bases and metal oxides as absorbents.

**Group II:** Designed to simultaneously extract H<sub>2</sub>S and organic sulfur compounds (such as COS, CS<sub>2</sub>, and mercaptans). These processes are primarily characterized by physical absorption.

## 2. Modification and Cation Exchange (Theoretical Background)

The efficiency of adsorbents like clinoptilolite can be significantly enhanced through chemical modifications:

1. Cation Exchange: Replacing Na<sup>+</sup> ions within the zeolite framework with other metal cations drastically alters the adsorption properties, improving selectivity for specific contaminants.

2. Decatination (Dealumination): The process of removing aluminum from the zeolite lattice (dealumination) modifies the heat of adsorption and enhances selectivity for certain molecules, such as CO<sub>2</sub>. This serves as a fundamental mechanism in acid modification processes.

### Liquid-Phase Purification Processes

- Chemisorption (Amine Scrubbing): This is the most common method for H<sub>2</sub>S removal. Aqueous solutions of organic bases—amines like MEA, DEA, MDEA, and DIPA—are used. Regeneration occurs in a reboiler at temperatures between 70-150 C.

- Physical Absorption: These processes use organic solvents where absorption capacity increases proportionally with partial pressure, making them economical for high-pressure gases with high concentrations of acid components. Key industrial processes include:

- Fluor (propylene carbonate).
- Purisol (N-methylpyrrolidone).
- Rectisol (methanol cooled to -30C).
- Selexol (dimethyl ether of polyethylene glycol).

Physico-Chemical Solvents: Mixed solvents like Sulfinol (sulfolane + DIPA + water) combine chemisorption and physical dissolution to treat gases containing both H<sub>2</sub>S and organic sulfur.

### 3. Clinoptilolite and High-Silica Zeolites (Material Characteristics)

Natural minerals such as clinoptilolite and mordenite are distinguished by their unique structural stability. These minerals are characterized by a high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (approximately 10). Acid resistance: zeolites with high silica content exhibit superior resistance to acidic environments. This makes them highly effective for the purification of acidic gases like H<sub>2</sub>S, as they maintain structural integrity during the adsorption-desorption cycles.

#### Oxidative and Alkaline Processes

- Oxidative Processes: These involve the liquid-phase oxidation of H<sub>2</sub>S into elemental sulfur. Examples include the Stretford (using ADA catalyst) and Tayioks processes. They are highly selective for H<sub>2</sub>S but are generally limited to small-scale operations (less than 10 tons of sulfur per day).

- Alkaline Processes: Used primarily for mercaptan removal. To improve the solubility of mercaptans, "solutizers" (organic additives like methanol or naphthenic acids) are added to the alkaline solutions.

### 4. Adsorption kinetics and dynamics (experimental/results section)

Understanding the dynamics of the adsorption process is essential for optimizing purification efficiency:

1. adsorption processes are typically conducted in stationary, moving, or fluidized adsorbent beds.

2. dynamic activity: the dynamic capacity of the adsorbent is directly influenced by the radii of its secondary pores (transport pores), which facilitate the diffusion of molecules.

3. impact of moisture: the presence of water vapor in the gas stream can impede the adsorption of target compounds. Due to competitive adsorption, water molecules may displace other components (e.g., CO<sub>2</sub> or sulfur compounds) from the active sites.

### 4. Adsorption Processes and Zeolites

- Industrial Adsorbents: While active carbons, silica gels, and alumina gels can be used, they often have low sulfur capacity due to the co-adsorption of heavy hydrocarbons.
- Synthetic Zeolites (Molecular Sieves): Zeolites are currently the preferred choice for sulfur removal because of their high affinity for polar molecules and their molecular-sieve properties.
- Zeolite Types and Selectivity:
  - NaA (4Å): Adsorbs H<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>3</sub>SH (methyl mercaptan) but excludes propane and larger molecules.
  - KA (3Å): Primarily used for dehydration, as it excludes ethane and larger molecules.
- Natural Zeolites: Recent interest has shifted toward natural zeolites due to their abundance and low cost. However, their industrial use is often limited by small pore sizes (approx. 4Å), necessitating chemical modification to expand their application in gas purification.

## 2. MATERIALS AND METHODS

The primary raw material used was natural clinoptilolite. To enhance its adsorption capacity, a chemical modification (acid treatment) method was employed.

### 2.1. Modification Process:

The zeolite samples were treated with hydrochloric acid (HCl) under varying conditions:

- Concentration: 0.5 to 10.0 N.
- Temperature: 20 °C to 90 °C.
- Duration: 2 to 10 hours.
- Solid-to-Liquid Ratio: 1:5.

### 2.2. Characterization:

The modification leads to dealumination—the selective removal of aluminum ions from the zeolite framework. This process was monitored to ensure the expansion of the "entry windows" of the pores without collapsing the crystalline structure.

## 3. RESULTS AND DISCUSSION

### 3.1. Structural Transformation

The study found that the degree of dealumination is the key factor determining the sorbent's efficiency. When the dealumination level reaches approximately 30-40%, the specific surface area and pore volume increase significantly. Beyond 40%, the structural integrity of the zeolite starts to degrade, leading to a decrease in mechanical strength.

### 3.2. Adsorption Dynamics

Experimental data indicates that acid-modified clinoptilolite shows a higher dynamic activity for H<sub>2</sub>S compared to its natural state.

- Isosteric Heat of Adsorption: The heat of adsorption for H<sub>2</sub>S and COS on modified clinoptilolite is lower than on synthetic NaX zeolites. This suggests that the regeneration of the adsorbent (desorption) can be achieved at lower temperatures, leading to significant energy savings.
- Mercaptan Removal: While natural clinoptilolite is ineffective for large molecules like methyl mercaptan, the modified version demonstrates a high degree of capture due to the expanded pore structure.

### 3.3. Pilot Testing

Industrial trials conducted at the Orenburg Gas Processing Plant confirmed that the modified clinoptilolite maintains its activity over multiple adsorption-regeneration cycles, proving its durability in harsh industrial conditions.

#### 4. ECONOMIC ANALYSIS

The production of modified clinoptilolite is highly cost-efficient. The technological flowchart includes standard industrial equipment: reactors, washing filters, dryers, and sifting units.

- Cost Comparison: The estimated cost of modified clinoptilolite is several times lower than that of synthetic 13X (NaX) zeolites.
- Scalability: The abundance of natural deposits ensures a stable supply chain for large-scale gas processing facilities.

#### 5. CONCLUSION

Acid modification (dealumination) is an effective method to tailor the pore structure of natural clinoptilolite for specific gas purification tasks. The modified sorbent achieves high-purity levels in removing H<sub>2</sub>S and organic sulfur compounds, meeting international pipeline standards. Lower regeneration energy requirements and lower production costs make modified clinoptilolite a superior alternative to synthetic adsorbents in the context of sustainable industrial development. Here is the literature review based on your document, translated into English for your article:

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