Acid Gas Removal by Super High Silica ZSM-5: Adsorption Isotherms of Hydrogen Sulfide, Carbon Dioxide, Methane and Nitrogen

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ABSTRACT: The adsorption of acid gas, including hydrogen sulfide and carbon dioxide by super high silica ZSM-5 was investigated. Equilibrium adsorption isotherms of high pure Hydrogen Sulfide and Carbon Dioxide were measured experimentally using this new sorbent. In addition, methane and nitrogen adsorption isotherms on this MFI-type zeolite were also measured as representative of other natural gas components. To enhance the reliability of the results, the adsorption pressure has been selected up to 20 bar at three different temperatures. Super high silica ZSM-5 for the adsorption of hydrogen sulfide shows an impressive result of 3.04 mmol.g\textsuperscript{-1} at 12 bar and 283K. This value was 2.69 mmol.g\textsuperscript{-1} for carbon dioxide at 21 bar and 283K. The adsorption capacity of H\textsubscript{2}S on the ZSM-5 is the highest and N\textsubscript{2} is the lowest, the order of adsorption capacity of components is H\textsubscript{2}S>CO\textsubscript{2}>CH\textsubscript{4}>N\textsubscript{2}. The adsorption heat of different adsorbates is calculated, 13.7 and 29.5 KJ.mol\textsuperscript{-1} for H\textsubscript{2}S and CO\textsubscript{2} respectively. Physical adsorption has occurred on high-silica ZSM-5, especially for hydrogen sulfide, and this is a great advantage. By increasing the temperature, the adsorption capacity of components on the ZSM-5 decreases but due to differences in adsorption heat of adsorbate, the ideal selectivity for hydrogen sulfide increases. There is a challenge in choice of the best condition for H\textsubscript{2}S removal, as, by increasing temperature, the adsorption capacity of hydrogen sulfide reduces, but the selectivity of the hydrogen sulfide increases as compared to other gases. This phenomenon is not true for the selectivity of other components.

Keywords: Adsorption: Acid Gas Removal; Hydrogen Sulfide; Super High Silica Zeolite; ZSM-5; Natural Gas Sweetening; Model of Adsorption;

1. INTRODUCTION.

Natural gas has less environmental pollution than other types of hydrocarbon sources. It is predicted that the production and consumption of natural gas will have an increasing upward trend for another 60 years with different scenarios\textsuperscript{1}. Presence of large amounts of carbon dioxide
and a small amount of hydrogen sulfide, so-called acid gas in the natural gas can cause several operational problems. For example, small amounts of hydrogen sulfide in the natural gas can lead to significant damage including catalyst poisoning, poor product quality, and environmental pollution. Many methods may be employed to remove acid gas (primarily H₂S and CO₂) from hydrocarbon streams. The available methods may be broadly categorized as those depending on chemical reaction, absorption, or adsorption. However, the adequate performance of Amines in industrial processes has been widely acknowledged by conventional gas plants, challenges are in the emergence and delivery of new methods that provide staff and environmental safety, also reduce capital and operational cost under various conditions with higher quality. The scope of this paper is research on gas sweetening, especially the development of ZSM-5 molecular sieve. The final deliverable is finding an appropriate zeolite with high selectivity and performance.

The use of adsorbents in the oil and gas industry is enhancing. Finding and overcoming existing industrial challenges will lead to the development of adsorbents for natural gas sweetening. Zeolites have the ability to separate gases due to their unique properties such as molecular sieve attributes, selectivity, chemical and physical stability and different adsorption capacity. Zeolites have been utilized successfully in the natural gas refinery plant for industrial separation processes such as dehydration, mercaptan and carbon dioxide removal. In natural gas sweetening, zeolites have not yet been industrialized. Zeolites with a very high Si/Al ratio and all-silica zeolites may help researchers come up with a commercially optimal solution. MFI-type zeolite is one of these adsorbents that seems to have suitable chemical and physical properties to adsorb acid gas. Super high silica ZSM-5 is theoretically effective in adsorbing hydrogen sulfide. There is little information in the literature about acid gas removal by ZSM-5 adsorbents, especially at high-pressure ranges. There is no available information about adsorption on ZSM-5 as MFI-type with a very high Si/Al ratio. Owing to the risks of hydrogen sulfide gas, scant available researches, have conducted at low concentrations and low pressures near the atmospheric. Therefore, it is not possible to provide a good view of this adsorbent to find a suitable adsorption model and selectivity.

In this article, adsorption of high pure hydrogen sulfide on Na-ZSM-5 with Si/Al=3000 is measured up to 12 bar, near the condensation point at three different temperatures. Due to the repeatability of the experiments, the results can be considered as a reference data. Also, this molecular sieve was investigated for the adsorption of carbon dioxide from natural gas at high pressures.

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¹ All pressures in this study are absolute
pressures. It is noted that few articles are known about the adsorption of CO₂ at high pressure on the ZSM-5 with a super high Si/Al ratio. Natural gas, in addition to hydrogen sulfide and carbon dioxide, contains other hydrocarbons such as methane which contains a major proportion among other hydrocarbons. There are also some nitrogen and inert gas which are usually present in natural gas. To study the selectivity of various natural gas components on ZSM-5, the adsorption isotherms of methane, carbon dioxide and nitrogen were measured up to 20 bar.

Adsorbed molecules are selected based on polarity and size upon the molecular sieve that has a regular lattice structure. The feed to gas plants is often included considerable amounts of H₂S (sour gas) or both H₂S and CO₂ (acid gas)⁶. The adsorption of hydrogen sulfide on H-ZSM5 and Na-ZSM5 was investigated by Garcia and Lercher using IR spectroscopy, and the surface chemistry was examined at equilibrium pressures of hydrogen sulfide up to 0.5 mbar; they found that Si-OH-Al bonds were formed, and molecular adsorption was observed in both zeolite (Na- and H-) ZSM-5⁷. It should be noted that identifying the mechanism of hydrogen sulfide adsorption on zeolites is a challenge during adsorption. The process is associated with the cations in the zeolite structure; oxygen impurities in the adsorbed phase of metal oxides in the zeolite cations that are outside the framework may form a chemical reaction and produce water. To understand the mechanism of adsorption, several MFI type like HZSM-5 and Na-ZSM-5, LTA-based zeolites inclusive of NaA, CaNaA, ZnNaA, MnNaA, CoNaA, NiNaA, and CuNaA and FAU-based zeolite systems for example NaX, NaY, and HY, have studied with IR method⁷,⁸, UV method⁹ and nuclear magnetic resonance (NMR)¹⁰. Yokogawa et al. prepared MFI (ZSM-5) and Ag-grafted MFI zeolites with Si/Al=24.9 to remove volatile sulfur compounds (VSCs) and compared their capacity in capturing H₂S for a very low H₂S concentration of 30 ppm at the near atmospheric pressure¹¹.

Due to the nature of hydrogen sulfide as toxic gas and consequently expensive set up of experimental rigs to maintain the safety of staff, few experimental studies with simple terms of pressure and composition have been performed to find ZSM-5 adsorption isotherms. In some other studies, a limited attempt has been made to simulate the H₂S adsorption on ZSM-5 zeolite. Theoretical approaches for removal of H₂S by Cosoli et al.¹² has made using Grand Canonical Monte Carlo (GCMC) simulation, where removal of hydrogen sulfide from biogas streams has been simulated using various zeolites such as FAU (NaX and NaY), LTA (zeolite A) and MFI, but they simulated the adsorption behavior at low pressures up to 1 kPa¹². The adsorption of hydrogen sulfide on seven all-silica zeolite frameworks (CHA, DDR, FER, IFR, MFI, MOR and
MWW) was simulated by Shah et al. for H$_2$S and CH$_4$, both pure and mixture components. The simulation was performed in a wide range of compositions, pressures and temperatures through Gibbs ensemble Monte Carlo simulations at high pressure up to 50 bar. They demonstrated that selectivity increases with increasing H$_2$S concentration due to suitable adsorbate-adsorbent interactions. MFI showed the highest degree of selectivity at high H$_2$S concentrations. The most favorable adsorption enthalpy is due to the optimal sorbent-adsorbate interactions. They also conducted a computational study on the adsorption of H$_2$S/CH$_4$ binary mixtures, the ideal adsorbed solution theory predicts properties for H$_2$S/CH$_4$ binary mixtures, but it has little accuracy in choosing between high-performance zeolites. The mentioned adsorbents allow optimal removal of H$_2$S for gas-phase adsorption; the selectivity of H$_2$S over H$_2$O for silicalite is close to 20 and is promising for sour gas sweetening even in the presence of moisture$^{13}$. Table 1 shows the saturation equilibrium adsorption results of hydrogen sulfide on different zeolites, for more information, can also refer to review articles$^{2,14,15}$ and view the results of dynamic adsorption and breakthrough test. It is important to note that in many adsorbents such as LTA (4A, 5A) and FAU (13X, 13Y), dissociative adsorption occurs. Dissociative adsorption is the reason for the high adsorption values in these adsorbents, which are irreversible and not regenerable.

**Table 1. Hydrogen sulfide adsorption on zeolites**

Since there is no experimental data about the adsorption of H$_2$S on ZSM-5 at high pressures using pure hydrogen sulfide; for applications to natural gas sweetening, therefore the experimental saturation adsorption isotherms of hydrogen sulfide and other components of natural gas focus of this work. It is noted that ZSM-5 with a super-high Si/Al ratio is a hydrophobic zeolite that has an excellent static adsorption capacity for hydrogen sulfide. At lower temperatures, the adsorption capacity of hydrogen sulfide on ZSM-5 increases, but the selectivity of hydrogen sulfide decreases.

**2. EXPERIMENTAL SECTION**

**2.1. MATERIALS**

ZSM-5 with Si/Al=3000 was purchased from Fuyu (Zhangjiagang) New Materials Technology Co. (China) as a super-high silica MFI type zeolite close to all-Silica zeolites. The basic specification of this zeolite is reported in Table 2 received by the vendor. High purity liquid hydrogen sulfide
with mass fraction purity of 0.999, carbon dioxide gas with mass fraction purity 0.9995, methane
gas with mass fraction purity of 0.9999, and nitrogen gas with mass fraction purity of 0.9999
were prepared.

Table 2. Specifications of Zeolites ZSM-5

2.2. EXPERIMENTAL SETUP and PREPARATION

To measure the equilibrium adsorption isotherms of H₂S, N₂, CO₂ and CH₄ at high pressures, an
adsorption experimental setup with a static volumetric method were designed and manufactured. In this method, the volume and temperature of the adsorption bed are constant, so the adsorption is calculated by measuring the pressure. This method of calculation of adsorption is simple, effective, and widely used. Despite the online temperature and pressure transmitters, the required information for calculations is easily available. Before the gas enters to adsorption bed, the mass of the gas is measured by volume, temperature and pressure, then the gas enters the bed and the injection dose is calculated; afterwards, equilibrium occurs and the adsorption value on the adsorbent is calculated. The sketch of the experimental setup is shown in Figure 1, all materials used to set up the equipment are stainless steel. A needle valve and a ball valve separate the storage compartment and the adsorption bed. The ball valve is used to isolate the chambers, and the needle valve is responsible for the injection rate. The adsorption setup has enough flexibility to operate at different temperatures and pressures. Temperature and pressure are measured and recorded with online transmitters with an accuracy of 0.001 bar for pressure and 0.1 K for temperature. A package including a circulator and constant temperature bath is used to regulate and maintain the temperature with an accuracy of 0.1 K. To vacuum making up to 3 mbar absolute, a vacuum pump is used. The adsorbent is calcined but samples were taken place in the furnace for 2 hours at a temperature of 670 K with an increasing temperature rate of 1K per minute, then while maintaining the zeolite temperature in the crucible with lid, weighed and placed inside the adsorption bed, then the volume is measured several times using helium. This is the amount of adsorption bed volume, regardless of the adsorbent volume. To prepare the bed for adsorption isotherms, the samples are vacuumed to 3 mbar absolute and equilibrated, then the adsorption isotherms are measured. After adjusting the temperature, the ball and needle valves are opened and a certain amount of gas enters the
adsorption bed. The amount of adsorption is calculated step by step by increasing the absolute pressure from 3 mbar. The condition of the next test is to create equilibrium for at least 30 minutes.

In this study, measuring the isotherm of pure gas at a certain pressure and temperature has a fundamental difference as compared with the work of the previous investigators\textsuperscript{17,18} that makes the higher accuracy in the measurements. i.e. after the storage compartment, a pressure and temperature transmitter are used (see Figure 1, items J and K) that does not need to weigh the storage compartment to find injection amount, the weight of the injected gas to adsorption bed is calculated with temperature and pressure of the storage compartment like the weight of gas inside the adsorption bed. By selecting the appropriate equation of state with the equilibrium temperature and pressure of storage compartment and adsorption beds, the moles of adsorbed gas are calculated as follows:

\[ n_{\text{ads}} = n_T - n_{eq} \]  \hspace{1cm} (1)

where \( n_{\text{ads}} \) is the adsorbed moles, the \( n_T \) and \( n_{eq} \) are injected and remaining moles of gas in the bed, respectively.

**Figure 1.** experimental setup sketching: (A) helium gas container; (B) process gas container (H2S, CO2, CH4, N2); (C) storage compartment; (D) temperature transmitter of adsorption bed; (E) pressure transmitter of adsorption bed; (F) adsorption bed; (G) constant temperature bath; (H) circulator; (I) vacuum pump; (J) pressure transmitter of storage compartment; (K) temperature transmitter of the storage compartment.

2.3. ADSORPTION MODELING.

The adsorption data of H\textsubscript{2}S, CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2} on the super-high silica were fitted on Langmuir, Freundlich, Sips and Toth isotherm models.

Freundlich isotherm is used to describe heterogeneous systems\textsuperscript{19}. This empirical equation defines the surface heterogeneity and the exponential distribution of active sites and their energies. Freundlich equation (2) can be written as in the following\textsuperscript{20}

\[ q = k_F p^{1/n} \]  \hspace{1cm} (2)

In this equation, \( k_F \) is the Freundlich constant and \( n \) is the constant that expresses the driving force of adsorption.
The Langmuir adsorption isotherm is another adsorption isotherm that simply assumes that adsorption takes place at specific homogeneous sites. The Langmuir equation is as follows (3)\(^2\)

\[
q = \frac{q_m bP}{1 + bP}
\]  
\((3)\)

The maximum number of adsorption sites on the adsorbent surface is expressed by \(q_m\) in terms of mmol. g\(^{-1}\) or g.g\(^{-1}\), and \(b\), as an adsorbent property, is the binding affinity of the adsorption sites. According to the Langmuir equation, if \(P\) is infinitely inclined, the total capacity of the monolayer is completed, the Langmuir equation is thermodynamically inconsistent because it has been proven that according to Gibbs thermodynamics, a plateau in the high-pressure range cannot exist\(^2\).

A well-known adsorption model is the Sips adsorption isotherm, which can be considered as a combination of Langmuir and Freundlich models. This isotherm is represented by the following nonlinear equation\(^2\) (4)

\[
q = \frac{q_m (bP)^{1/n}}{1 + (bP)^{1/n}}
\]  
\((4)\)

Like the Langmuir equation, the maximum number of adsorptions is shown by \(q_m\) in terms of mmol.g\(^{-1}\) or g.g\(^{-1}\), and \(b\) is the Langmuir constant, related to the energy of adsorption sites and the Freundlich exponent represents by \(n\).

Another empirical equation that was developed to improve the Langmuir isotherm is Toth isotherm model. Toth is a three-parameter equation and a useful model for describing heterogeneous adsorption systems. Toth isotherm design to meet low and high concentration boundaries that express as follow\(^2\) (5)

\[
q = \frac{q_m bP}{[1 + (bP)^{t}]^{1/t}}
\]  
\((5)\)

The maximum adsorption capacity represented by \(q_m\), the adsorption affinity represented by \(b\) and \(t\) is the Toth constant.

The Toth and Sips isotherm contains three parameters and Freundlich and Langmuir contain two; therefore, Toth and Sips can describe most of the experimental data better than the two-parameter models. All models were tested with 95% confidence, and isotherm parameters were obtained through a nonlinear fit of experimental data with the mentioned model equations.

To model the process, various error functions are defined to evaluate and fit the isotherm equations with the experimental data. Sum Square of Errors (ERRSQ), Correlation Coefficient (r), Coefficient of Determination (\(R^2\)), Standard Error, Hybrid Fractional Error Function (HYBRID),
Marquardt’s Percent Standard Deviation (MPSD), Average Relative Error (ARE) and Sum of Absolute Errors (EABS) are error functions that have been used in various articles\(^\text{22}\). In this paper, in addition to \(r\) and \(R^2\), AICc as a mixed model was calculated to compare and choose the best model. The AICc is a modified mixed model of Akaike Information Criterion (AIC)\(^\text{23}\) corrected for small sample sizes. The AICc is used as an accurate and reliable statistical analysis\(^\text{24}\) to examine the convergence of experimental data and models. The Akaike Information Criterion (AIC) is a mathematical method that quantitatively evaluates the compatibility of a model with data. The AICc is an estimator of prediction error and relative quality of statistical models for selecting the best model. Under the data fitting conditions, the optimal fitted function or model must be selected among several alternatives with the criteria which the decision is based on; lower AICc values indicate a better data fitted model\(^\text{24}\), a model with a delta-AICc (the difference between the two AICc) of more than -2 is considered statistically significantly better than the models that are being compared to\(^\text{25}\). Therefore, with AICc, the best model among different models of curve fitting can be scored and selected.

2.4. ISOSTERIC HEAT of ADSORPTION

The isosteric adsorption heat of gases on solids is considered as an important parameter for interpreting the adsorption behavior on porous materials, which can provide unique and useful information about the interaction between the adsorbate and adsorbent surface and the distribution of energetic sites, helps to understand the mechanism of adsorption. This parameter is used to calculate energy balance and temperature changes in the industrial adsorption beds. On an industrial scale, the heat of adsorption increases the temperature of the bed and affects the adsorption process. In principle, from the thermodynamic point of view, the isosteric heat of adsorption is the difference between the molar enthalpy in the gas phase and the differential enthalpy in the adsorbed phase (Eq. 6)\(^\text{26}\).

\[
q_{st} = h_g - \left[ \frac{\partial H^E}{\partial n^E} \right]_r
\]  

\(H^E\) is the specific enthalpy in terms of \((\text{J.g}^{-1})\) and \(n^E\) is the given adsorption value in terms of \((\text{mol.g}^{-1})\), both are Gibbs excess variables. With proper adsorption isotherms and modeling, the heat of adsorption can be obtained. In principle, one of the most famous relationships that simplifies equation 6 at the ideal gas state, is the Clausius–Clapeyron relation for a one-component adsorption system. This formula is as follows\(^\text{26}\).
\[ q_{st} = -R \cdot \left[ \frac{\partial \ln P}{\partial (1/T)} \right]_{nE} \]  

(7)

To find the isosteric adsorption heat, a series of adsorption isotherms measured at different temperatures, a linear regression of \( \ln P \) versus \( 1/T \) gives a linear slope of \(-q_{st}/R\) in the constant coverage fraction. Repeating this slope in different surface coverage gives the isosteric heat of adsorption as a function of coverage\(^{26}\). Using two adsorption isotherms, isosteric heat can be obtained, which is better to be \( \Delta T \approx 20K \) (the greater the temperature difference, the greater the calculation error). It has been suggested to use a slope with three points to increase the accuracy of calculations, three adsorption isotherms with \( \Delta T = 10K \) cause a statistically significant increase in calculations\(^{27–29}\).

3. RESULTS and DISCUSSION

3.1. CHARACTERIZATION

Physical adsorption is a powerful method to analyze the structure of porous materials, using volume data of adsorbed gas on the surface of porous material at different relative pressures. With the advent of devices based on physical adsorption, useful information obtains with different theories such as volume, specific surface area, and size distribution of cavities. Measuring the total surface area of an impermeable material that has a stable shape is not difficult, but in the case of samples with a porous structure, there are problems in determining the total surface area and porosity. BET is a method for accurately measuring the total area of samples based on the adsorption of some molecular species in a gaseous state on the adsorbent surface. Nitrogen adsorption-desorption, Surface Area (BET), and Pore Size Determination (BJH) were used to analyze the structure of ZSM-5 (Figure 2 and Figure 3 related to nitrogen adsorption-desorption isotherms and pore size distribution, respectively. The parameters obtained from the nitrogen adsorption-desorption are given in Table 3 which approve vendor specification.

<table>
<thead>
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<th>Table 3. Tested specifications of super high silica ZSM-5 by ( \text{N}_2 ) adsorption-desorption</th>
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Figure 2. \( \text{N}_2 \) adsorption−desorption isotherms at 77 K; circles symbols, adsorption and squares symbols, desorption on the super high silica ZSM-5
3.2. STATIC EQUILIBRIUM ADSORPTION MEASUREMENTS.

For application in natural gas sweetening, adsorption isotherms of hydrogen sulfide, carbon dioxide, methane, and nitrogen were measured at three different temperatures 283, 293, and 303 K. These measurements are made by the adsorbent saturation method, the adsorption capacity \( q \) expressed in terms of \( \text{mmol}_{\text{adsorbate}}/\text{g}_{\text{adsorbent}} \), that is expressed as a function of absolute pressure at a fixed temperature.

Hydrogen sulfide adsorption isotherms up to 12 bar are shown in Figure 4. The Sips model has the best fitted result among the proposed models according to table 4 based on the AICc analysis. The Sips model has a significant difference with other models at 293 and 303 K and the difference between Sips, Toth and Langmuir at 283 K is not statistically significant. The Sips model is shown as round dots in Figure 4.

\[
\text{Figure 4. H}_2\text{S adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Sips model.}
\]

\[
\text{Table 4. Data fitting with statistical model results}
\]

The equilibrium data of CO\(_2\) adsorption as a competitor of H\(_2\)S are measured and shown in Figure 5. The adsorption isotherms are measured up to 20 bar at three different temperatures and were modelled with four models. Toth model is the best fitted model based on AICc analysis (Table 4), which is shown as round dots in Figure 5.

\[
\text{Figure 5. CO}_2\text{ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Tammanloo et al. data at 303K\textsuperscript{26}; red multiplication sign, Hefti et al. data at 298 K\textsuperscript{31}.}
\]

For methane gas, which has the largest share of hydrocarbon components in the natural gas, the adsorption isotherms are also measured up to 20 bar and is shown in Figure 6. According to Table 4, the best-fitted model is the Toth. At 283 K, according to the AICc analysis, there is no
statistically significant difference between the Toth and Sips model, at 293 and 303 K according to the same analysis. The Toth model (round dots in Figure 6) is better fitted with the experimental data.

Figure 6. CH₄ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Tammanloo et al. data at 303K.

Nitrogen is colorless, odorless, tasteless, and considered as an inert gas at normal temperatures and pressures, which is usually notable in sour gas. Therefore, the adsorption of this gas on the ZSM-5 was investigated at different temperatures up to 20 bar. In Figure 7, these data were plotted for nitrogen. For nitrogen isotherms also, adsorption models were examined as reflected in Table 4. The results of the Sips and Toth are almost similar. According to AICc analysis, the Toth model is slightly more consistent with the experimental data. This model is shown in Figure 7 in the form of round dots.

Figure 7. N₂ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Hefti et al. at 298 K.

It is recommended that the selection of the best adsorption model be done after calculating the adsorption heat, which is discussed and finalized in Section 3.4. The isotherms of CO₂, CH₄, and N₂ are well matched with the data in other articles to 20 bar, this study shows that carbon dioxide adsorption increases with increasing Si/Al ratio. In another study, the adsorption of CH₄ and CO₂ were measured up to 10 bar and 303 K, which is entirely consistent with the measurements of this work. For a better evaluation, these results are compared in Figure 5 for CO₂ and in Figure 6 for CH₄. In another investigation by Hefti et al., the adsorption of carbon dioxide and nitrogen on ZSM-5 was investigated, which is illustrated in Figures 5 and 7 for CO₂ and N₂ respectively at 298 K and up to 10 bar. In the present research, the measured experimental data have good repeatability. The validation of hydrogen sulfide adsorption isotherms is not possible due to the non-existence of high-pressure experimental data. However, from the validity and repeatability of other components’ adsorption on ZSM-5, it can be concluded that H₂S
Isotherms have good accuracy and are reliable. Adsorption of hydrogen sulfide, carbon dioxide, methane, and nitrogen on super high silica ZSM-5 according to the IUPAC classification are normal type I\textsuperscript{19}. The capacity at low pressures has a sharp upward trend, and after increasing the pressure, the slope of the adsorption diagram decreases. Class I adsorption isotherms can be described by the Langmuir equation. The characteristic of this type of isotherm is the horizontal line that represents the maximum amount of adsorption ($q_m$). In this category, with increasing pressure to very high pressures, there is no change in the maximum amount of adsorption. These isotherms indicate microporous material adsorbents, that don’t cover multilayer adsorption.

Most adsorbents are heterogeneous, so their binding properties cannot be simply modeled using the Langmuir isotherm. The Freundlich isotherm is also commonly used to model adsorption in the sub-saturated region. Freundlich considers an exponential distribution of adsorption sites, so overall, it cannot express the properties of the actual bond under saturation conditions or higher concentrations. On the other hand, the Toth and Sips isotherms model the binding properties between adsorbate and adsorbent in the whole isotherm, which is efficient in the saturated and sub-saturated regions\textsuperscript{21}. The selected models are Sips for H$_2$S and Toth for CO$_2$, CH$_4$, and N$_2$, other models excepted Freundlich, also have $R^2$ close to one. Table 4 summarizes the review and analyze the experimental data. According to very low delta AICc between Sips and Toth models, Toth isotherm is also suitable for H$_2$S and can interpret the results. Toth parameters for each adsorbent were given in Table 5. The primary characteristic of the Langmuir isotherm is an assumption that only a single layer forms, meaning there is saturation (a horizontal asymptote) once monolayer capacity is reached\textsuperscript{34}. Owing to the Toth model being adapted from Langmuir, this assumption also applies. In the adsorption isotherms of all mentioned gases on ZSM-5, with increasing temperature, the maximum saturated adsorption ($q_m$) decreases on the adsorbent surface at all adsorption pressures, which indicates physical adsorption\textsuperscript{34}. The adsorbate occupies the binding site on the adsorbent surface, the adsorbent-adsorbate competitive process at the binding site on adsorbent is indicated by $b$; higher values of $b$, indicate stronger adsorbate–adsorbent interactions, and show a higher activity coefficient in zeolite bound and a free site which especially occurs at a lower temperature. The higher value of $b$, increase the preferable concentration of adsorption sites and the higher the mean binding energy and vice versa. Decreasing $b$ significantly reduces the mean binding energy with significant differences in the distribution of affinity. Toth heterogeneity parameter, $t$, is close to one for ZSM-5 which indicates that the adsorbent is homogeneous. Al atoms have a significant effect on
heterogeneity, which is shown by the difference in \( t \)-values, with an increase in \( t \) value, the mean binding energy decreases since the number of aluminum atoms in the super-high silica zeolite is minimal, so the \( t \) numbers are close to one.

Table 5. Toth parameters and Henry’s constant (KH) of each adsorbate on the super high silica ZSM-5

In this adsorbent, \( t \) value is almost constant and close to one as can be seen in Table 5, where \( b \) has the highest value for \( H_2S \) and decreases from \( H_2S, CO_2, CH_4 \) and \( N_2 \) respectively. Therefore adsorbate–adsorbent interactions reduce from \( H_2S \) to \( N_2 \). The reduction of mean binding energy is slightly different between \( H_2S \) and \( CO_2 \), but it is remarkable as compared to \( CH_4 \) and \( N_2 \). To determine the adsorption of different components and compare them with each other, Figure 8 shows the adsorption isotherms of all four adsorbents at 293K and it clearly demonstrates that the adsorption of the mentioned component on ZSM-5 is as the following ranking order: \( H_2S > CO_2 > CH_4 > N_2 \).

Figure 8. adsorption isotherms at 293K; blue tilted squares, \( H_2S \); red squares, \( CO_2 \); green triangles, \( CH_4 \); orange circles, \( N_2 \); round dots, Toth model; solid line, Sips model.

3.3. ISOETRIC HEAT of ADSORPTION

The adsorption evaluation is usually measured based on two characteristics: adsorption isotherm and adsorption heat. The isotherm measures the adsorption capacity, and the adsorption heat indicates the strength of the interactions between the adsorbent surface and the adsorbate\(^{35}\). IsostERIC heat is the ratio of very small changes in the adsorbate enthalpy to small changes in the amount of adsorption. Theoretically in the homogeneous porous material, the heat of adsorption is constant and not dependent on the loading, which means that the mobility of the adsorbed molecules does not affect the interaction of adsorbent atoms and adsorbed molecules, a direct sign of surface heterogeneity is the reduction of isoSTERIC heat of adsorption by loading. Molecules prefer to be adsorbed at sites that have the highest adsorption energy, and as adsorption continues, the molecules are adsorbed at lower energy sites and the adsorption heat is reduced\(^{32}\).
To enhance reliability of results, the isosteric heat of H$_2$S on the ZSM-5 was calculated according to Equation 7 in three temperatures of 283, 293 and 303 K. These calculations were performed with the two isotherms: Toth and Sips, which had the best data fitting results on the isotherms (Figure 9). According to Sips Equation, the $Q$ as the heat of adsorption is equal to the amount of isosteric heat in the fractional loading of 0.5, while the $Q$ parameter in the Toth equation is equal to the isosteric heat in the fractional loading of zero. We believed that the $q_{st}$ is temperature independent and the corresponding average temperature was defined as Eq. 8

$$T_{avg} = \frac{3}{\left(\frac{1}{T_1} + \frac{1}{T_2} + \frac{1}{T_3}\right)}$$

Here $T_{avg} = 293K$ and according to Table 5, at this temperature, half of the maximum loading value ($q_m$) is 1.49 mmol.g$^{-1}$. From the Figure 9, we can see that the amount of isosteric heat of adsorption in the fractional loading of 0.5 is 14.5 kJ.mol$^{-1}$ for Sips model, and in the fractional loading of zero is 13.7 kJ.mol$^{-1}$ for Toth model, which are well close to each other. These values are theoretically equal to the heat of adsorption ($Q$) of hydrogen sulfide on the ZSM-5. The adsorption heat of other compounds is calculated in the same way and are presented in Table 6. Since the experimental equations of Sips and Toth are well consistent with the equilibrium data, isosteric heat as a loading function can be used to select the appropriate isotherm model for hydrogen sulfide. The heat of adsorption, calculated by Sips and Toth are well matched as also mentioned in Section 3.2. Although the performance of Sips and Toth are not very different from each other, Sips model is a better choice for hydrogen sulfide due to better-fitting according to AICc analysis. Using the same approach, the choice of Toth isotherm for other compounds is also confirmed. Error values as shown in Table 6 are 0.7, 0.4, 0.7 and 0.1 for H$_2$S, CO$_2$, CH$_4$ and N$_2$ respectively at zero loading. The error is in the acceptable range and not much change is expected for isothermal heat values.

Table 6. Heat of adsorption ($Q$) on super high-silica ZSM-5

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Adsorption ($Q$)</th>
</tr>
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<tr>
<td>H$_2$S</td>
<td>14.5 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>13.7 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>13.7 kJ.mol$^{-1}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>13.7 kJ.mol$^{-1}$</td>
</tr>
</tbody>
</table>

Figure 9. Isosteric heat of adsorption of H$_2$S, CO$_2$, CH$_4$ and N$_2$ on super high silica ZSM-5;
We have two broad categories of adsorption, which are physical adsorption and chemisorption, which depends on the surface forces. The intermolecular forces of Van der Waals are characteristic of physical adsorption, while the interactions in chemisorption are stronger and involve degrees of electron transfer or electron sharing such as the formation of a chemical bond. In general, the energy of chemisorption is significantly higher than physical adsorption\textsuperscript{36}. Due to the low adsorption heat of the tested component on the super high silica ZSM-5, physical adsorption has occurred, especially for hydrogen sulfide. This is a great hopefulness because most conventional industrial zeolites, such as LTA (4A, 5A) and FAU (13X, 13Y), have dissociative adsorption. Repeatability of tests, specifically for hydrogen sulfide several times after complete vacuum regeneration, confirms the regenerability and physical adsorption of this adsorbent after hydrogen sulfide adsorption.

The isosteric heat of adsorption versus loading is given in Figure 9 for all compounds. This type of isosteric heat trend, which does not decrease significantly with increasing loading, indicates the homogeneity\textsuperscript{32} of the high-silica ZSM-5, which has already been deduced in the interpretation of adsorption isotherms (see section 3.2). In principle, the energy of the adsorption sites in this adsorbent is uniform, because in the adsorption process, the adsorbate first tends to adsorb on the sites that have the most energy, and as the adsorption continues, the molecules are then adsorbed on less energetic sites and the isosteric heat decreases. The increase in isosteric heat value in high loadings is due to the tendency of fluid molecules to be adsorbed together at high pressure, and condensation heat due to fluid-fluid ($q_{f-f}$) interactions as adsorptive-adsorptive intermolecular forces occurring during adsorption\textsuperscript{26}. During the adsorption, with increasing loading, the behavior of isosteric heat shows that the adsorption process is controlled by non-specific interaction heat due to fluid-solid ($q_{f-s}$) interactions as dispersion forces\textsuperscript{26}.

3.4. COMPONENT SELECTIVITY.

Pure gas equilibrium adsorption and comparison between different gases is the first estimate to find an adsorbent with suitable adsorption potential. Dynamic adsorption test has a higher cost than static, so ideal selectivity is use as an appropriate tool for screening adsorbents before dynamic adsorption tests. Ideal selectivity also called, Henry’s selectivity at a constant temperature, can be written as follows\textsuperscript{37}.

$$\alpha_{n,m} = \frac{K_n}{K_m}$$  \hspace{1cm} (9)
In this equation, \( n \) and \( m \) are components, \( K_n \) and \( K_m \) are Henry’s constant of \( n \) and \( m \) respectively. Henry’s constants for each adsorbent are given in Table 5; Henry’s constant provides an idea of relative preference near-zero loading. This constant determines and indicates the adsorbent tendency in the adsorption process. Henry’s law at low-pressure express as follows:

\[
\lim_{P \to 0} \frac{q}{P} = K_H
\]  

(10)

The ideal selectivity for the gas components at different temperatures was calculated and listed in Table 7. According to Table 5, the maximum amount of adsorption (q_m) decreases with increasing temperature, which was also shown in the isotherm diagrams, but the ideal selectivity for hydrogen sulfide to other compounds increases with increasing temperature. This effect of temperature on the selectivity of hydrogen sulfide to carbon dioxide is more significant. It is noted that this relationship is not valid for CO₂/CH₄ and CO₂/N₂ as well as methane to nitrogen (CH₄/N₂); therefore, there is a challenge in choosing the optimal condition of adsorption, for hydrogen sulfide, the adsorption decreases with increasing temperature, but the selectivity increases.

Table 7. ideal selectivity on ZSM-5

The separation factor is expressed as \( R_L = 1/(1 + b \cdot C_0) \), which evaluates the favorability of an adsorption system, where \( C_0 \) represents the initial concentration of adsorbate and \( b \) is adsorption affinity. The lower \( R_L \) is the more desirable the adsorption process is. In general, the adsorption process is favorable when \( R_L \) is less than 1.\(^{38}\) Considering Ideal Adsorbed Solution Theory (IAST)\(^ {34}\) in the separation factor function, amount of ideal selectivity depends directly on the affinity of adsorption. The affinity of a fluid component for an adsorbent depends on the molecular structure such as size, shape, polarity and temperature of the system. Table 5 shows the adsorption affinity values (\( b \)), it can be seen that at 283K, the adsorption affinity of carbon dioxide is higher than hydrogen sulfide, so it has a higher selectivity. By increasing temperature this ratio is reversed and selectivity of hydrogen sulfide increases. The reasons that the affinity of hydrogen sulfide and other compounds changes with temperature is due to the adsorption heat of various compounds (calculated in Section 3.3). Therefore, to study more precisely the selectivity behavior of compounds, it is necessary to study the heat of adsorption.
The adsorption affinity is according to the following formula used in the Toth and Sips isotherms:\(^{32}\)

\[ b = b_\infty \exp\left(\frac{Q}{R_g T}\right) \quad (11) \]

Here \( b_\infty \) is the adsorption affinity constant at infinite temperature, therefore, according to this relation, the \( b \) is dependent on temperature and decreases with increasing temperature (can be seen in Table 5). According to Eq. 11, lower adsorption heat reduces the effect of temperature on affinity. Table 6 illustrate the heat of adsorption \( (Q) \) for hydrogen sulfide is less than other compounds. The other compounds have almost the same \( Q \) and with increasing temperature, less decrease in the adsorption affinity \( (b) \) for hydrogen sulfide is seen compared to other compounds. For carbon dioxide at the lowest test temperature (283 K), the binding affinity of the adsorption sites shows a higher value than hydrogen sulfide, but this ratio changes above 289 K with linear calculation. Therefore, with the advancement of affinity, selectivity also increases.

The adsorbents require sufficient adsorption capacity and good separation efficiency, and selectivity aids in decision making. Using a binary mixture is a short cut to study the separation of a gas’s component at different pressures. A model selectivity at higher pressures was employed which is according to the ideal adsorbed solution theory (IAST), and equation (12) is used for this purpose:\(^{34}\)

\[ S = \frac{q_i}{q_j} \frac{p_i}{p_j} \quad (12) \]

\( S \) is selectivity, \( i-j \) represent components and \( q \) is adsorption at partial pressure \( P \). Selectivity of \( \text{CO}_2/\text{CH}_4, \text{CO}_2/\text{N}_2, \) and \( \text{CH}_4/\text{N}_2 \) at 293 K with the IAST model are shown in Figure 10. This method is speculation without considering binary experimental studies, but it is given to measure the similarity of the calculations of this study with the other work. In some previous studies, the selectivity for the methane, nitrogen, and carbon dioxide on ZSM-5 were calculated by IAST\(^{34,39}\) and also, binary experimental methods\(^{30}\) was calculated for selectivity \( \text{CO}_2/\text{CH}_4 \) on ZSM-5(Figure 10, orange squares), for a better evaluation, these results are presented in Figure 10 in conjunction with the data obtained under this research, which well matched with our present results. There is missing research on the selectivity of hydrogen sulfide over other compounds, so considering the compatibility of selectivity and equilibrium adsorption with the other mentioned researches for \( \text{CO}_2, \text{CH}_4, \) and \( \text{N}_2 \), this model can be extended confidently to the
selectivity of hydrogen sulfide over other compounds, H$_2$S selectivity on ZSM-5 are illustrated in Figure 11.

Figure 10. CO$_2$, CH$_4$ and N$_2$ selectivity on ZSM-5 by IAST method; dark blue dashed line, CO$_2$/N$_2$; dark green round dotes, CH$_4$/N$_2$; orange solid line, CO$_2$/CH$_4$; blue tilted squares, CO$_2$/N$_2$ by Wang et al.\textsuperscript{34}; green circles, CH$_4$/N$_2$ by Yang et al.\textsuperscript{39}; brown triangles, CO$_2$/CH$_4$ by Yang et al.\textsuperscript{39}; orange squares, CO$_2$/CH$_4$ by Tammanloo et al.\textsuperscript{30}

Figure 11. H$_2$S selectivity on ZSM-5 by IAST method; dark green round dotes, H$_2$S/N$_2$; brown dashed line, H$_2$S/CH$_4$; blue solid line, H$_2$S/CO$_2$; green circle, ideal selectivity of H$_2$S/N$_2$(Table 7); brown triangle, ideal selectivity of H$_2$S/CH$_4$(Table 7); blue square, ideal selectivity of H$_2$S/CO$_2$ (Table 7).

4. CONCLUSIONS

For application in the natural gas sweetening process, to find a suitable adsorbent, the equilibrium adsorption isotherms of hydrogen sulfide and carbon dioxide were measured as acid gas. The isotherms of methane and nitrogen were also calculated as other components of natural gas on ZSM-5. Super high silica ZSM-5 demonstrates a promising result in adsorbing acid gas with low heat of adsorption. The adsorption capacity of H$_2$S is the highest and N$_2$ is the lowest, the order of adsorption capacity at all temperatures is H$_2$S>CO$_2$>CH$_4$>N$_2$.

Due to the deadly risk of handling hydrogen sulfide and high cost to set up a proper laboratory for this kind of study, the most available data in the literature are focused on low pressure or low concentration systems, therefore, proper information on the behavior of adsorbents in high pressures are not available. At the higher pressure the more accurate adsorption models, fit on the experimental data. Therefore, the test pressures in this study have been selected so high (20bar) that the adsorption behavior of high silica ZSM-5 can be well analyzed.

After precise adsorption modelling with 95% confidence, the selectivity of different adsorbates on this adsorbent was investigated. The selectivity of acid gas (H$_2$S, CO$_2$) is high compared to other gases, but the main challenge is the selectivity of hydrogen sulfide relative to carbon dioxide, the selectivity of hydrogen sulfide to other components, especially to carbon dioxide, increases with increasing temperature. To obtain a higher uptake of hydrogen sulfide than carbon dioxide, a higher temperature is more desirable, however, it should be noted that at higher
temperatures, the adsorption capacity decreases. Ideal selectivity is influenced by affinity, for carbon dioxide at the lowest test temperature (283 K), the binding affinity of the adsorption sites shows a higher value than hydrogen sulfide, but this ratio changes above 289 K, so the selectivity of hydrogen sulfide to carbon dioxide above this temperature is in favor of hydrogen sulfide. By isosteric heat calculation, the reason for affinity behavior was investigated, which refers to the different heat of adsorption of hydrogen sulfide (13.7 KJ.mol⁻¹) and carbon dioxide (29.5 KJ.mol⁻¹).

Due to the low adsorption heat, physical adsorption has occurred on high-silica ZSM-5, especially for hydrogen sulfide, this is promising because most conventional industrial zeolites, such as LTA (4A, 5A) and FAU (13X, 13Y), have dissociative adsorption. Repeatability of tests, specifically for hydrogen sulfide several times after complete vacuum regeneration, confirms the regenerability and physical adsorption of this adsorbent after hydrogen sulfide adsorption.

**ASSOCIATED CONTENT**

Supporting information

This information is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).

The experimental equilibrium adsorption data of hydrogen sulfide, carbon dioxide, methane and nitrogen on the super high silica ZSM-5 at three temperatures 283, 293 and 303 K along with computational uncertainties are summarized in the tables S1-S4.

5. REFERENCES


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Table 5. Toth parameters and Henry’s constant (K_H) of each adsorbate on the super high silica ZSM-5
Table 6. Heat of adsorption (Q) on super high-silica ZSM-5
Table 7. Ideal selectivity on ZSM-5
Table 1. Hydrogen sulfide adsorption on zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Adsorption Value of H₂S (mmol.g⁻¹)</th>
<th>Reference</th>
</tr>
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<td>5A</td>
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</tr>
<tr>
<td>SAPO-43</td>
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<td>CuX</td>
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Table 2. Specifications of Zeolites ZSM-5

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<td>Chemical composition</td>
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<td>Na₂O</td>
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<td>Particle size distribution</td>
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<td>Crystallinity</td>
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<td>Pore volume</td>
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<td>Micropore volume (T-Plot)</td>
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<td>Average pore diameter (4V/A by BET)</td>
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Table 3. Tested specifications of super high silica ZSM-5 by N2 adsorption-desorption

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<th>Item</th>
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<td>Micropore volume (T-Plot)</td>
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Table 4. Data fitting with statistical model results

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<th>Model</th>
<th>Temp. (°C)</th>
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<th>Toth</th>
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Table 5. Toth parameters and Henry's constant ($K_H$) of each adsorbate on the super high silica ZSM-5

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<tr>
<th>adsorbate</th>
<th>H$_2$S</th>
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<th>CH$_4$</th>
<th>N$_2$</th>
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<td>283</td>
<td>293</td>
<td>303</td>
<td>283</td>
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<td>q</td>
<td>3.16</td>
<td>2.98</td>
<td>2.78</td>
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<td>b</td>
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<td>$K_H$</td>
<td>4.70</td>
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Table 6. Heat of adsorption ($Q$) on super high-silica ZSM-5

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<tr>
<th>Component</th>
<th>Heat of Adsorption (KJ.mol$^{-1}$)</th>
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<tbody>
<tr>
<td>H$_2$S</td>
<td>13.7 ± 0.7</td>
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<td>29.5 ± 0.4</td>
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<td>CH$_4$</td>
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<td>N$_2$</td>
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Table 7. Ideal selectivity on ZSM-5

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<td>CH$_4$/N$_2$</td>
<td>3.84</td>
<td>3.97</td>
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</table>
List of Figures

**Figure 1.** experimental setup sketching: (A) helium gas container; (B) process gas container (H₂S, CO₂, CH₄, N₂); (C) storage compartment; (D) temperature transmitter of adsorption bed; (E) pressure transmitter of adsorption bed; (F) adsorption bed; (G) constant temperature bath; (H) circulator; (I) vacuum pump; (J) pressure transmitter of storage compartment; (K) temperature transmitter of storage compartment.

**Figure 2.** N₂ adsorption–desorption isotherms at 77 K; circles symbols, adsorption and squares symbols, desorption on the super high silica ZSM-5.

**Figure 3.** Pore size distribution of super high silica ZSM-5; circles symbols, adsorption.

**Figure 4.** H₂S adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Sips model.

**Figure 5.** CO₂ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Tamnanloo et al. data at 303K; red multiplication sign, Hefti et al. data at 298 K.

**Figure 6.** CH₄ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Tamnanloo et al. data at 303K.

**Figure 7.** N₂ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Sips model.

**Figure 8.** Adsorption isotherms at 293K; blue tilted squares, H₂S; red squares, CO₂; green triangles, CH₄; orange circles, N₂; round dots, Toth model; solid line, Sips model.

**Figure 9.** Isosteric heat of adsorption of H₂S, CO₂, CH₄ and N₂ on super high silica ZSM-5.

**Figure 10.** CO₂, CH₄ and N₂ selectivity on ZSM-5 by IAST method; dark blue dashed line, CO₂/N₂; dark green round dots, CH₄/N₂; orange solid line, CO₂/CH₄; blue tilted squares, CO₂/N₂ by Wang et al.; green circles, CH₄/N₂ by Yang et al.; brown triangles, CO₂/CH₄ by Yang et al.; orange squares, CO₂/CH₄ by Tamnanloo et al.

**Figure 11.** H₂S selectivity on ZSM-5 by IAST method; dark green round dots, H₂S/N₂; brown dashed line, H₂S/CH₄; blue solid line, H₂S/CO₂; green circle, ideal selectivity of H₂S/N₂ (Table 7); brown triangle, ideal selectivity of H₂S/CH₄ (Table 7); blue square, ideal selectivity of H₂S/CO₂ (Table 7).

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2 Additional experimental data of figures are available in the Supplementary data as table;
Figure 1. Experimental setup sketching: (A) helium gas container; (B) process gas container (H₂S, CO₂, CH₄, N₂); (C) storage compartment; (D) temperature transmitter of adsorption bed; (E) pressure transmitter of adsorption bed; (F) adsorption bed; (G) constant temperature bath; (H) circulator; (I) vacuum pump; (J) pressure transmitter of storage compartment; (K) temperature transmitter of storage compartment.

Figure 2. N₂ adsorption–desorption isotherms at 77 K; circles symbols, adsorption and squares symbols, desorption on the super high silica ZSM-5
Figure 3. Pore size distribution of super high silica ZSM-5; circles symbols, adsorption.

Figure 4. H₂S adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Sips model.
Figure 5. CO$_2$ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Tamnanloo et al. data at 303K$^{30}$; red multiplication sign, Hefti et al. data at 298 K$^{31}$.

Figure 6. CH$_4$ adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Tamnanloo et al. data at 303K$^{30}$. 
Figure 7. \( \text{N}_2 \) adsorption isotherms; blue tilted squares, 283K; red squares, 293K; green triangles, 303K; round dots, Toth model; yellow small circles, Hefti et al. at 298 K\textsuperscript{31}.

Figure 8. Adsorption isotherms at 293K; blue tilted squares, H\textsubscript{2}S; red squares, CO\textsubscript{2}; green triangles, CH\textsubscript{4}; orange circles, N\textsubscript{2}; round dots, Toth model; solid line, Sips model.
Figure 9. Isosteric heat of adsorption of H$_2$S, CO$_2$, CH$_4$ and N$_2$ on super high silica ZSM-5.

Figure 10. CO$_2$, CH$_4$ and N$_2$ selectivity on ZSM-5 by IAST method; dark blue dashed line, CO$_2$/N$_2$; dark green round dots, CH$_4$/N$_2$; orange solid line, CO$_2$/CH$_4$ blue tilted squares, CO$_2$/N$_2$ by Wang et al$^{34}$; green circles, CH$_4$/N$_2$ by Yang et al$^{39}$; brown triangles, CO$_2$/CH$_4$ by Yang et al$^{39}$; orange squares, CO$_2$/CH$_4$ by Tamnanloo et al$^{30}$. 
Figure 11. H₂S selectivity on ZSM-5 by IAST method; dark green round dots, H₂S/N₂; brown dashed line, H₂S/CH₄; blue solid line, H₂S/CO₂; green circle, ideal selectivity of H₂S/N₂ (Table 7); brown triangle, ideal selectivity of H₂S/CH₄ (Table 7); blue square, ideal selectivity of H₂S/CO₂ (Table 7).