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Evaluation of molecular sieve degradation in the natural gas drying process by TSA

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Abstract

Drying is one of the most important stages in processing industrial gas streams since humidity often disrupts the performance of subsequent unit operations. The natural gas dehydration is commonly carried out by adsorption using hydrophilic porous materials by Temperature Swing Adsorption (TSA). Thermal swings, along with the presence of other contaminants, may lead to adsorbent degradation and thus reduce the lifespan of the drying process. The objective of this study was to assess the hydrothermal stability of a molecular sieve used in natural gas drying through an aging test that simulates the operating conditions of a typical TSA. Textural properties and water adsorption capacity were monitored during the heating/cooling cycles. It was observed that the textural properties decrease as the material undergoes aging cycles, and this impacts the water adsorption capacity and, consequently, the performance of the material to be applied in the natural gas dehydration process.

Keywords: natural gas; molecular sieve; drying; aging

1. Introduction

Natural gas processing is a crucial stage in the oil and gas production process, and it is favored as an energy source because it generates fewer residues compared to other fossil fuels, leading to a projected increase in global consumption. The primary component of natural gas is methane, typically comprising between 75% and 90% of the mixture. However, it also contains other hydrocarbons like ethane, propane, and butane, along with impurities such as water, carbon dioxide, nitrogen, and hydrogen sulfide [1].

The presence of water vapor and/or free water can cause several issues during processing, transportation, and storage [2]. Water in natural gas decreases its calorific value, thus reducing its efficiency as a fuel. Additionally, condensed water in pipelines diminishes the effective area, resulting in decreased transport capacity. It can also exacerbate corrosion, especially when combined with acidic gases such as carbon dioxide and hydrogen sulfide. The most severe problem is that condensed water can lead to the formation of hydrates, causing blockages in pipelines and other relevant equipment [3].

Conventionally, the removal of moisture from natural gas in offshore installations is carried out in fixed-bed adsorption units with Temperature Swing Adsorption (TSA) processes using adsorbents with high adsorption capacity and high selectivity for water [4-6]. However, while these properties are desirable for adsorbents, their regeneration requires high temperatures to be effective.

One of the main practical problems in the TSA process is the reduced performance of the adsorbent when subjected to repeated thermal cycles. The deactivation or aging of the material leads to a loss of adsorption capacity and/or an increase in mass transfer resistance, usually resulting from coke formation or loss of crystallinity [7].

During thermal regeneration, the sieve is exposed to a combination of high temperature and high humidity, under which conditions slow and

irreversible breakdown of the crystalline structure can occur [8].

Coke formation occurs in applications where reactive hydrocarbons are exposed to high temperatures during the desorption (regeneration) stage. Coke results from secondary reactions or the deposition of impurities on the external surface, which can poison active sites or block access to them by reacting molecules [9]. Regardless of the system, it is important to limit the deactivation rate of the material, and for this, it is essential to understand how this deactivation occurs.

Given the above, the main objective of this study is to verify the aging of molecular sieves used in natural gas processing. For this purpose, a sample of a commercial molecular sieve was subjected to several adsorption/desorption cycles through temperature variation and some characteristics of the adsorbent material were analyzed.

2. Material and methods

2.1 Aging tests

Figure 1 shows the experimental apparatus used for testing the aging of molecular sieves. The unit consists essentially of a reactor (Parr Instrument Company, USA), where the sieve is confined under controlled temperature and pressure conditions, and a boiler to humidify the sample. More details of the apparatus can be found in previous work [10, 11].

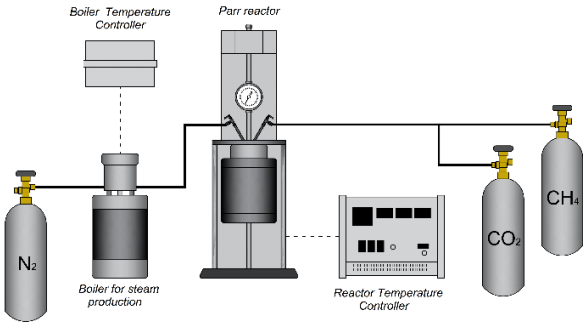

Fig. 1. Experimental unit for aging tests.

The first step was to weigh the fresh sample and place it in the reactor. The system was maintained at 30 °C while the sample was humidified under a continuous flow of N_2 (1 bar gauge) bubbled through water for 24 hours. After humidification, liquid n-heptane (0.6 mL per gram of sample) was added to reproduce the heavy fractions of natural gas that may condense during processing. The closed system was then pressurized to 30 bar with a CO_2/CH_4 mixture in a molar ratio of 1:4. The pressure was maintained at 30 bar for 1 hour to simulate the adsorption step. Following this, cycles of heating (from 30 to 250 °C) and cooling (from 250 to 30 °C) were performed with each complete cycle (heating and cooling) lasting 12 hours.

2.2 Characterization

Textural properties, such as specific surface area, pore volume and micropore volume, were determined from nitrogen adsorption isotherms at −196 °C using an Autosorb-iQ3 (Quantachrome Instruments, USA). Prior to the measurements, the samples were outgassed at 300 °C for 12 h under vacuum of 10^{-6} bar. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation, the total pore volume was determined at a relative pressure of 0.95, and the micropore volume was determined using the Dubinin-Radushkevich (DR) equation [12].

The water vapor isotherms were measured using an Intelligent Gravimetric Analyzer—IGA (Hiden Isochema Ltd., UK). Water vapor was generated using liquid deionized water placed in a vial, which was degassed by repeated evacuation to achieve the desired water vapor pressures. More details of this equipment are found elsewhere [11]. Prior to isotherm measurements, the sample was degassed at 300 °C under vacuum (10^{-6} mbar) for 12 h. In the adsorption/desorption experiments, pressure ranged between 0.1 and 70 mbar at 40 °C.

The model proposed by Aranovich-Donohue Model was used to fit water vapor adsorption isotherms for the studied samples [13]. The monolayer expression was represented by the Sips equation [14]

3. Results

Figure 2 shows the N_2 adsorption/desorption isotherms at -196 °C for samples subjected to different numbers of aging cycles.

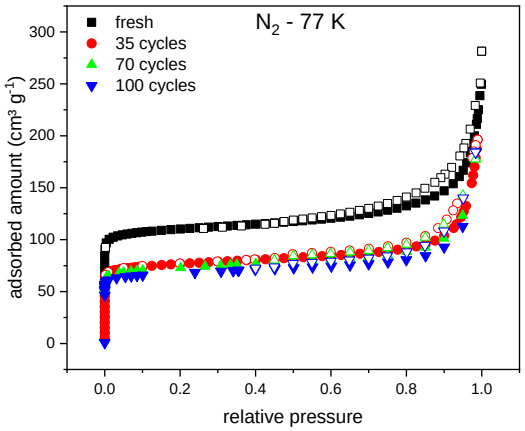

Fig. 2. N_2 adsorption/desorption isotherms at -196 °C.

The textural properties of the samples, obtained from the isotherms in Figure 2, are shown in Table 1.

Table 1. Textural properties.

Sample	S_{BET} (m^2/g)	V_P (cm3/g)	V_{MP} (cm3/g)
Fresh	398	0.28	0.16
35	300	0.23	0.11
70	284	0.19	0.11
100	266	0.17	0.11

It is observed that all surface area values of the aged samples are below the value observed for the fresh sample. However, it is noticeable that the decrease is more intense in the first cycles. The results show that when subjected to 35 aging cycles, the surface area decreases by 25% compared to the virgin sample, but only a 4% loss in area is observed with an additional 35 aging cycles. A similar trend is observed for the total pore volume, indicating that there is pore obstruction.

Regarding the micropore volume, it is observed that a minimum value is reached within the first 35 cycles evaluated and remains unchanged up to 100 cycles. This suggests that aging has a greater impact on the pores outside the region assessed by this methodology.

Water isotherms were obtained to evaluate the water adsorption capacity of the fresh and aged samples over the cycles. These results are shown in Figure 3.

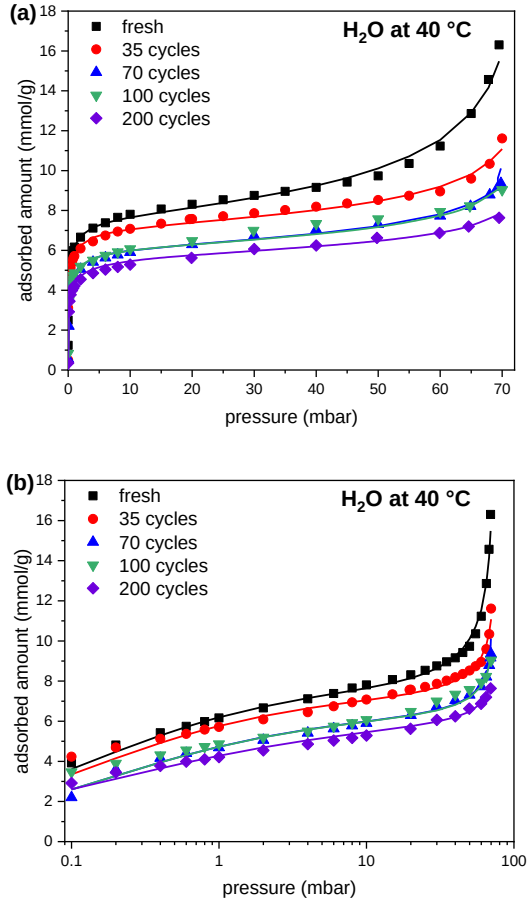

Fig. 3. Water vapor isotherms at 40 °C in linear (a) and logarithmic (b) scales. Symbols represent the experimental data and continuous lines are fits to the Aranovich-Donohue model.

It is possible to observe that the materials have a high capacity for water adsorption even at low pressures, evident by the rectangular shape of the isotherm for the fresh material. A plateau on the adsorbed load is observed in the pressure range of 10 - 40 mbar. This behavior is the same for the samples after several aging cycles, however, over the cycles, the water adsorption capacity decreases gradually.

Using 30 mbar pressure as an example, the adsorption capacity decreases by 10% after the sample undergoes 35 aging cycles compared to the fresh sample. After 70 cycles, the material loses 23% of its capacity and maintains a similar capacity after 100 cycles. However, the sample with 200 cycles had its adsorption capacity reduced by only 13% compared to the sample with 100 cycles, indicating that the water adsorption capacity

decreases more significantly during the initial cycles.

Experimental data from all isotherms were adequately fitted by the Aranovich-Donohue model with calculated parameters summarized in Table 2.

Table 2. Aranovich-Donohue parameters.

Sample	q_{max} (mmol g^{-1})	b (mbar^{-1})	n	e
Fresh	7.850	7.800	0.634	0.243
35	7.350	7.555	0.633	0.146
70	6.349	5.541	0.623	0.139
100	6.349	5.540	0.620	0.135
200	6.110	5.500	0.495	0.105

As observed in the isotherms in Figure 3, the Aranovich model fits the experimental data well and can represent the water vapor adsorption capacity for these samples. However, at low pressures, a greater discrepancy between the experimental and calculated data is identified. Through the model parameters, it is possible to confirm that, as aging cycles occur, the interaction with water decreases.

The q_{max} parameter indicates a maximum adsorption capacity, b accounts the adsorbent-adsorbate interaction, n is qualitatively related to the homogeneity of the adsorbent surface and e it is an empirical constant. All parameters show a decreasing trend as the aging advances.

4. Conclusions

The main conclusion of this work is that, although many aging cycles are required to observe drastic changes in water adsorption capacity, the initial cycles can already indicate the performance of the material to be used in the natural gas drying process by TSA. This can be useful in developing a material evaluation procedure for decision-making in the process.

Acknowledgements

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References

[1] Baker RW, Lokhandwala K. Natural Gas Processing with Membranes: An Overview. Industrial & Engineering Chemistry Research. 2008;47:13.

[2] Mokhatab S, Poe WA, Mak JY. Natural Gas Dehydration. Handbook of Natural Gas Transmission and Processing2015. p. 223-63.

[3] Yang Y, Wen C, Wang S, Feng Y. Theoretical and numerical analysis on pressure recovery of supersonic separators for natural gas dehydration. Applied Energy. 2014;132:248-53.

[4] Webley PA. Adsorption technology for CO2 separation and capture: a perspective. Adsorption. 2014;20:225-31.

[5] Huang HY, Yang RT, Chinn D, Munson CL. Amine-Grafted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas. Industrial & Engineering Chemistry Research. 2003.

[6] Farag HAA, Ezzat MM, Amer H, Nashed AW. Natural gas dehydration by desiccant materials. Alexandria Engineering Journal. 2011;50:431-9.

[7] Crittenden B, Thomas W. Adsorption Technology and Design1998.

[8] Ruthven DM. Principle of Adsorption and Adsorption Processes1984.

[9] Guisnet M, Costa L, Ribeiro FR. Prevention of zeolite deactivation by coking. Journal of Molecular Catalysis A: Chemical. 2009;305:69-83.

[10] Gomes Santiago R, Ferreira dos Santos B, Gomes Lima I, Oliveira Moura K, Carrijo Melo D, Mantovani Grava W, et al. Investigation of premature aging of zeolites used in the drying of gas streams. Chemical Engineering Communications. 2018;206:1367-74.

[11] Nascimento BO, dos Santos BF, Maia DAS, de Melo DC, Vilarrasa-Garcia E, Torres AEB, et al. Water adsorption in fresh and thermally aged zeolites: equilibrium and kinetics. Adsorption. 2021;27:1043-53.

[12] Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistry. 2015;87:1051-69.

[13] Aranovich; GL, Donohue MD. A new approach to analysis of multilayer adsorption. Journal of Colloid and interface science. 1995;173:6.

[14] Maia DAS, Azevedo TM, Pereira DS, Castro RAM, Nascimento BO, Rodríguez-Castellón E, et al. Water vapor adsorption on small pore ion-exchanged zeolites. Adsorption. 2024;30:507-17.