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Synthesis of 5A molecular sieve for hydrogen purification in pressure swing adsorbers

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Abstract: 5A molecular sieve is used in petroleum and gas industries as an adsorbent, especially for hydrogen purification. In this study, 5A molecular sieve for hydrogen purification in pressure swing adsorber (PSA) is synthesized, and its physical properties are reported. At the first stage, the 4A zeolite powder produced as the precursor of 5A zeolite is prepared using hydrothermal method with the molar ratio of $SiO_2/Al_2O_3 \approx 1.5$, and then kaolin powder as binding agent is used for preparing extrudates. Then, these pellets were converted to 5A type through ion exchange process using calcium chloride solution. After determining physical properties, adsorption tests for the separation of CH_4 and CO from a feed stream (H_2=89.9 mol%, CH_4= 10 mol%, and CO=0.1 mol%) under severe operating conditions (P=40atm, T=40°C, and GHSV from 1200 to 1750 h^{-1}) are carried out in a laboratory scale fixed-bed adsorber. Results show that the synthesized 5A molecular sieve has acceptable physical properties in comparison to data reported in literature. Moreover, a breakthrough time about 27 sec can be expected.

***Keywords*:** Adsorption, Molecular sieve 5A, Pressure swing adsorption (PSA), Hydrogen

Introduction

Molecular sieves have widespread applications in petrochemical and refining industries due to their unique adsorption, ion-exchange, and sieving properties. These materials are classified based on the nature of physical-chemical properties i.e., ion-exchange, density, porosity, shape and adsorption capacity. They have uniform small pores about 2 to 50nm which improves the selectivity, ion exchange, adsorption, and also optimize costs particularly. Molecular sieves are crystalline metal aluminosilicates having a three dimensional interconnecting network of silica and alumina tetrahedral. There are several methods to synthesis molecular sieves such as hydrothermal method considered as the most important technique. 5A molecular sieve (LTA ion-exchanged with Ca2+) is often utilized for the purification of gas streams. Moreover, it can be used to separate N-hydrocarbons from branched and polycyclic ones. Carter et al used the 5A and 4A molecular sieve to adsorb carbon dioxide and nitrogen in 1974[1]. Mofarahi and Gholipour [2] used molecular sieves to separate mixtures of gases (CO2 and CH4) in their studies. Rutherford [3] also used 5A molecular sieve to capture CO2 from mixture. Furthermore, in 2008, Grice et al [4] applied 5A to separate N- alkanes from crude oil. Production of pure hydrogen from a gas mixture containing 60–90 mol% hydrogen is an interesting subject in the petrochemical and oil refining industries. Pressure swing adsorption (PSA) is the most relevant approach to produce pure hydrogen using 5A molecular sieve. This process is designed to produce a dry hydrogen-rich product stream at the feed gas pressure containing 98–99.999 mol% H2 with a H2 recovery of 70–90%.

This contribution presents a route to synthesize 5A molecular sieve for hydrogen purification. After measuring the physical and chemical properties of the prepared molecular sieve, its dynamic behavior in a fixed-bed column under the industrial operating conditions is studied.

Materials and method

To synthesis the 5A molecular sieve for hydrogen purification, the following material are needed: Al2(Si)2O5(OH)4 (Merck), NaOH (Merck), sodium silicate 30%, CaCl2 (Merck), (NH4)2SO4 and H2SO4 96% (Merck). Sodium aluminate was mixed with water, aluminium oxide and sodium hydroxide in a magnetic stirrer as the first step. Then, the water, sulfuric acid and Tetra-n-butyl ammonium bromide added, and they were stirred to obtain a complete dissolution. Now, 24 ml of sodium silicate added into it for 10 minutes, and pH of the reaction mixture was also adjusted to about 11. Next, it was stirred for 45 minutes in the mixer as long as a gel was formed. After that, the obtained mixture was put into an oven at 150°C for 2 days. Gelatinous material turned to powder form after 2 days, and it was placed at room temperature for 2 hours. This prepared powder was then washed with deionized (DI) water until it neutralized. Finally, the obtained material was put into a furnace under nitrogen atmosphere under the temperature program of 25°C to 100 °C (4 °C/min), 100 °C to 500 °C (10 °C/min), and remained at 500 °C for 7 hours.
Zeolite powder produced by the proposed method was mixed with a desired weight of kaolin and distilled water, and stirred gently until thick slurry was prepared. Then, it was dried till the water content reach to 40%, and is passed through a home-made extruder. The spaghettis were dried at room temperature for one day, and then they were ion exchanged using one molar calcium chloride solution. Finally, the laboratory experiments were carried out using a pressure swing adsorber (PSA) set-up which was designed and constructed by the

Hengye Molecular Sieve Company. This installation consists of one cylindrical vertical column, heat exchanger, thermostat, mass flow controller system, gas chromatographer, valves for gas flow velocity adjustment and devices of measuring and control for temperature and flow. Adsorption process was realized in a fixed bed under dynamic conditions with the geometrical parameters of H = 0.15 m, and D = 2.95×10−2m. The feed used for performing experiments was composed of H_2=89.9 mol%, CH_4= 10 mol%, and CO=0.1 mol%. The pressure and temperature of the process were 40 atm and 40°C, respectively.

Results and Discussion

The specifications of the 5A molecular sieve pellets are presented in Table 1. It was observed that these specifications, and also X-ray diffraction pattern (XRD) of synthesized 5A powder were similar to corresponding ones revealed in the literature [5].

Table 1. Adsorbent specification

Specifications	Unit	Value
Crush strength	N	35 (Min.)
Diameter	mm	1.4-2.7
Bulk density	g/ml	0.72 min
Particle density	g/ml	1.09
Attrition	wt.%	0.33 max

The breakthrough curve obtained from the experiments, are shown in Fig. 1. This figure demonstrates the variation of hydrogen purity versus time in the output of the column at three level of feed flow rate. From these results, it can be concluded that the prepared 5A molecular sieve can selectively adsorb the CH_4 and CO impurities from the feed to produce pure hydrogen with the desired specification (>99.99%) under the severe operating conditions.

This results also indicates that as the gas hourly space velocity (GHSV) is increased, the breakthrough time is decreased conversely such that at GHSV=1200, 1600 and 1750 h^{-1}, the breakthrough times are 27, 19, and 17 sec, respectively. Since the adsorption capacity of the molecular sieve is limited by the number of shaped pores, it is speculated that by increasing the GHSV, the active pores are rapidly filled by the CH_4 and CO molecules, so a short time breakthrough is happened.

Conclusions

According to the physical, chemical and laboratory scale operational tests, it can be claimed that the proposed method to synthesize 5A molecular sieve can be nominated as a recipe to produce commercial 5A molecular sieve for hydrogen purification in PSA plants. However, comparing results with the commercial molecular sieves manufactured by the well-known companies such as Axens and UOP, and studying the effect of binder on sieving/adsorption properties are recommended for future works.

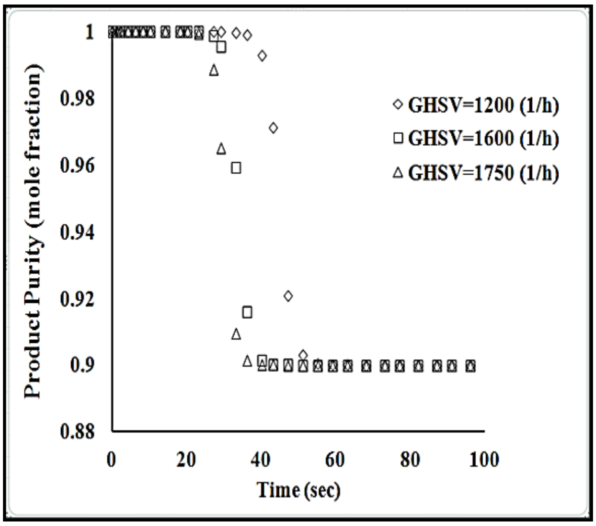

Figure 1. Breakthrough curve for the purification of H_2 using 5A molecular sieve, at 40 atm and 40°C

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