Synthesis of zeolite X from oil well drill cuttings for CO_2 capture

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Resumo/Abstract

RESUMO – Um dos resíduos mais abundantes do processo de exploração de gás natural e petróleo é o cascalho de perfuração. Neste trabalho, o cascalho de perfuração de poços foi estudado como matéria prima sustentável para a síntese de zeólito X, que é um excelente adorvente empregado para capturar CO_2. A análise elementar da amostra de cascalho por fluorescência de raios X revelou um material rico em SiO_2 (52,91%) e Al_2O_3 (17,95%). O processo de síntese foi realizado em três etapas: (i) tratamento hidrotérmico do cascalho em NaOH 8 mol L^{-1} a 200°C por 20 h, originando hidroxicancrinita (CAN); (ii) solubilização da hidroxicancrinita com HCl 37% e reciclagem do líquido alcalino obtido na etapa "i" para ajuste do pH em 14; e (3) cristalização hidrotérmica a 100°C por 44 h. O material obtido ao final do processo apresentou topologia faujasita (FAU) com elevada área superficial BET (632 $m^2.g^{-1}$) e capacidade de captura de CO_2 de 12,6% (2,864 $mmol.g^{-1}$). Esses resultados indicam que esta é uma rota sustentável para aproveitamento deste resíduo da indústria de petróleo para mitigar as emissões de CO_2.

Palavras-chave: Sustentabilidade, cascalho de perfuração, Captura de CO_2, zeólito X.

ABSTRACT – One of the most abundant waste products from the natural gas and oil exploration process is drill cuttings. In this work, drill cuttings were studied as a sustainable raw material for synthesizing zeolite X, an excellent adsorbent used to capture CO_2. Elemental analysis of the cuttings sample by X-ray Fluorescence revealed a material rich in SiO_2 (52.91%) and Al_2O_3 (17.95%). The synthesis process was carried out in three steps: (i) hydrothermal treatment of the cuttings in 8 $mol.L^{-1}$ NaOH at 200°C for 20 h, yielding hydroxycancrinite (CAN); (ii) solubilization of hydroxycancrinite with 37% HCl and recycling of the alkaline liquid obtained in step "i" to adjust the pH to 14; and (3) hydrothermal crystallization at 100°C for 44 h. The material obtained at the end of the process presented faujasite topology (FAU) with a high BET surface area (632 $m^2.g^{-1}$) and a CO_2 capture capacity of 12.6% (2.864 $mmol.g^{-1}$). These results indicate that this is a sustainable route for using this residue from the oil industry to mitigate CO_2 emissions.

Keywords: Sustainability, drill cuttings, CO_2 capture, zeolite X.

Introduction

With the increase in oil and natural gas production, there has also been an increase in waste generation from well drilling. Depending on the case, this waste can cause environmental impacts due to its composition, which contains heavy metals, hydrocarbons, and radioactive elements (1-3).

The cuttings generated during oil well drilling have a large amount of silica and alumina in their composition. This makes this waste a promising raw material for zeolite production (1-4).

Zeolites are microporous crystalline aluminosilicates whose three-dimensional structure is built from TO_4 tetrahedral units (T = Si or Al). These materials have been widely investigated as adsorbents, ion exchangers, and catalysts (5). In particular, zeolites with LTA (zeolite A) and FAU (zeolites X and Y) topologies have been used in CO_2 capture (6).

In this context, this work transforms drilling well cuttings into zeolite X with the aim of applying this material in CO_2 adsorption studies.

Experimental

Zeolite synthesis

The zeolite was synthesized in three steps: (i) Alkaline activation of the gravel, NaOH and water mixture at 200°C for 20 h in an autoclave to solubilize the silica; (ii) Acid dissolution: The solid obtained in the previous step was mixed with water and treated with 37% HCl at 80°C for 60 min under stirring; and (iii) Alkaline precipitation and crystallization: In the acid dissolution, the alkaline liquid recycled in the first step was also added until pH ≈ 14, followed by hydrothermal treatment at 100°C for 44 h. The materials were characterized by TG, SEM, XRD, XRF and textural analysis by N_2 physisorption.

CO_2 adsorption by TG

The TSA method was performed by thermogravimetric analysis using a Shimadzu DTG-60H instrument. The test schedule consists of the following steps: (i) Drying of the material at 350°C for 30 min under N_2 flow (100 mL.min^{-1}); (ii) Cooling to 30°C under N_2 flow (100 mL.min^{-1}); (iii) Introduction of a gas mixture CO_2: N_2 = 1:1, for 30 min, with a total flow of 100 mL min^{-1}; and (iv) The gas was exchanged for N_2 at a flow rate of 100 mL.min^{-1}, and the sample was heated to 200°C for desorption.

Results and Discussion

Characterization of the materials

Thermogravimetric analysis revealed significant mass loss in the drill cuttings (16.42%) and in the NaX zeolite (15.37%), associated with dehydration and loss of adsorbed gases. Elemental analysis of the cuttings showed 52.9% SiO_2 and 17.9% Al_2O_3, indicating the potential of the material as a precursor for zeolite production. The X-ray diffractogram confirmed crystalline phases as hydroxycancrinite and NaX zeolite (FAU topology), while electron microscopy highlighted typical morphologies for each material.

The N_2 adsorption isotherms of gravel are classified as mixed between type II and IV (loop H3) and the NaX zeolite as type I (loop H4) (7). The zeolite demonstrated a high micropore area (632 m^2.g^{-1}) and a predominance of pores in the 1.0–1.5 nm (0.2456 cm^3.g^{-1}). Textural properties highlighted a significant increase in the surface area of the synthesized zeolite (632 m^2.g^{-1}) compared to gravel (42 m^2.g^{-1}), reinforcing its potential as an adsorbent for CO_2 capture.

CO_2 adsorption by TG

The curve obtained in the study of the CO_2 adsorption/desorption capacity of the synthesized NaX zeolite is shown in Figure 1. In the adsorption process, the zeolite presented an adsorption capacity of around 12.6% of CO_2, indicating that the synthesized material presents an adsorption capacity (2.864 mmol.g^{-1}) close to other materials described in the literature (6).

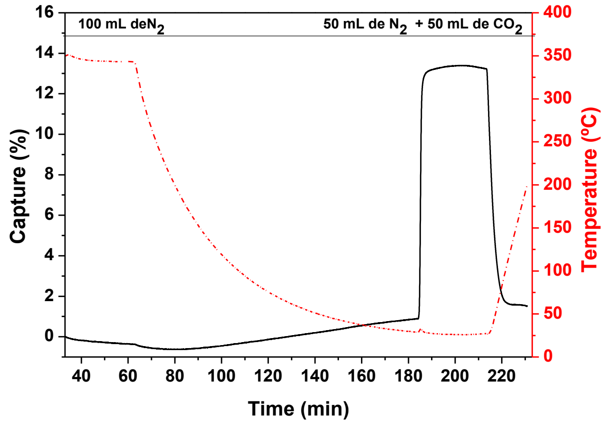

Figure 1. CO_2 adsorption-desorption curves of the synthesized zeolite through TSA.

Conclusions

The study demonstrated that it is feasible to use oil well drilling cuttings as a sustainable precursor for synthesizing zeolite X, with potential application in CO_2 capture. The three-step synthesis methodology allowed the production of zeolite X (faujasite topology) with high surface area (632 m^2.g^{-1}), adequate porosity (0.2456 cm^3 g^{-1}) and high carbon dioxide adsorption capacity (12.6% or 2.864 mmol.g^{-1}).

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