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Synthesis of mesoporous silica type SBA-15 from rice husk ash for application as adsorbent support in direct air capture

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Abstract

Due to the serious environmental consequences caused by the emission of greenhouse gases, the development of technologies and materials for application in CO_2 capture are encouraged. One of the possibilities is the use of high-performance solid adsorbents synthesized from industrial wastes, such as mesoporous silica type SBA-15 synthesized from rice husk ash. This material can be applied as a porous support for subsequent impregnation of amines, combining the good properties of both in relation to the process and working towards the development of a low-cost and environmentally suitable adsorbent. Within an experimental planning, the present work proposes using rice husk ash to obtain sodium silicate, which was applied as raw material for the synthesis of mesoporous silica. Once obtained, these supports were characterized in terms of chemical composition, textural properties and FTIR bands, in order to confirm their quality. Finally, its potential for application as a support was preliminarily evaluated with 60% TEPA-type amine impregnation and obtained a CO_2 adsorption capacity of 1.70 mmol/g under atmosphere of 7% CO_2. Future tests will be carried out using 400 ppm of CO_2 in the presence of moisture.

Keywords: Rice Husk Ash; Mesoporous silica SBA-15 type; Adsorbents for CO_2 capture.

1. Introduction

Carbon dioxide (CO_2) is a well-acknowledged greenhouse gas that has been increasingly contributing to global warming and climate change [1,2]. Amine scrubbing is one of the most mature technologies to CO_2 capture applied in large-scale processes [3,4]. However, some drawbacks of this technology prevent its spread and the adsorption based on solid adsorbents is a possible alternative potential [5,6].

In this context, the immobilization of amine-containing compounds on solid porous supports has attracted considerable attention in the last decades [3,4,7,8]. Amine-modified solid adsorbents combine the high affinity of amines towards CO_2 along with suitable textural properties and thermal stability of porous materials [1].

Inorganic and organic porous materials, including zeolites, silicas, metal-organic frameworks (MOFs), and activated carbons, have been extensively investigated as supports for amine impregnation. The mesoporous silica SBA-15-type is the most applied among them [6,7,9,10].

The silica SBA-15 by itself didn't presents a significant CO_2 adsorption capacity. But as related for some authors, like Henao et al. [7], the adsorption capacity can be rise of 0.11 mmol/g to 1.40 mmol/g by applying 40% of PEI in this support. Another example is the obtained by Zhang et al. [11] that improve the adsorption capacity of 0.61 mmol/g to 5.39 mmol/g in the with 60 % TEPA impregnation.

Besides it, the silica SBA-15 can be synthesized applying industrial wastes, such as coal ash and agricultural waste, like rice husk ash, what is really interesting in the economic and environmental point of view [7,12].

In this context, the synthesis of silica SBA-15 type using sodium silicate produced applying ash from burning rice husks is proposed, where its main characteristics as a porous support for the development of this high-performance adsorbents will be evaluated.

2. Materials and methods

An experimental planning was prepared, being carried out with the traditional commercial reagent

(TEOS - tetraethyl orthosilicate) for method validation. Then TEOS was replaced by sodium silicate (Na_2SiO_3) synthesized from the alkaline leaching of rice husk ash (RHA).

To obtain Na_2SiO_3, RHA is ground and subjected to leaching process according to the procedure described by Da Cruz [13]. Using a Paar reactor at constant stirring (100 rpm), the RHA remained for 3 hours in contact with NaOH solution (3 M) at 100 °C and 1 bar. The adopted solution/RHA ratio was 3:1.

The synthesis of SBA-15 is proposed in accordance with what was developed by Viola et al. [14], and occurs as shown in the flowchart presented in Figure 1 and according the steps described below:

1 – Addition of 20 g of template Pluronic P123 (Polyethylene glycol) in 750 mL of hydrochloric acid (HCl) 1.7 M, under stirring and at room temperature, until completely dissolved.

2 – The silicon source was added in the solution to aging step for 24 hours at 25 °C.

3 – The result solution was transferred to a Teflon reactor and send to hydrothermal reaction at 100 °C for 24 h.

4 – The final product was filtered, washed and then dried in an oven at 80 °C for 12 h.

5 – Finally, the silica was calcined at 550 °C for 1 h to eliminate the template.

According mass balance, the synthesis using TEOS used 42.5 g, and the synthesis using Na_2SiO_3 used 70 g of solution.

Within the tests carried out in the experimental planning, the directed (P123)/silica and acid volume/director (P123) ratios, aging time and hydrothermal occurrence were varied. Some of these tests are presented in Table 1.

Table 1. Experimental planning to SBA-15 obtention.

Sample	HCl solution (M)	Ratio HCl/ P123	Aging Condition
TEOS	1,7	5,32	Stirring, 24 h
Na_2SiO_3-3	1	3,13	Stirring, 24 h
Na_2SiO_3-9	1	3,13	Stirring, 3 h
Na_2SiO_3-11	1	3,13	Static, 24 h

Characterizations

The RHA was characterized in terms of the majority chemical composition (FRX) to determine the SiO_2 content present. The sodium silicate obtained was characterized using a titrimetric method to determine the Na_2O and SiO_2 contents present.

The SBA-15 samples were characterized in terms of major chemical composition (FRX), textural properties (BET) and main formation bands (FTIR). As preliminary tests, samples were evaluated regarding their CO_2 adsorption capacity using TGA-DSC in an atmosphere of 7% CO_2. Future tests will be carried out using 400 ppm of CO_2 in the presence of moisture.

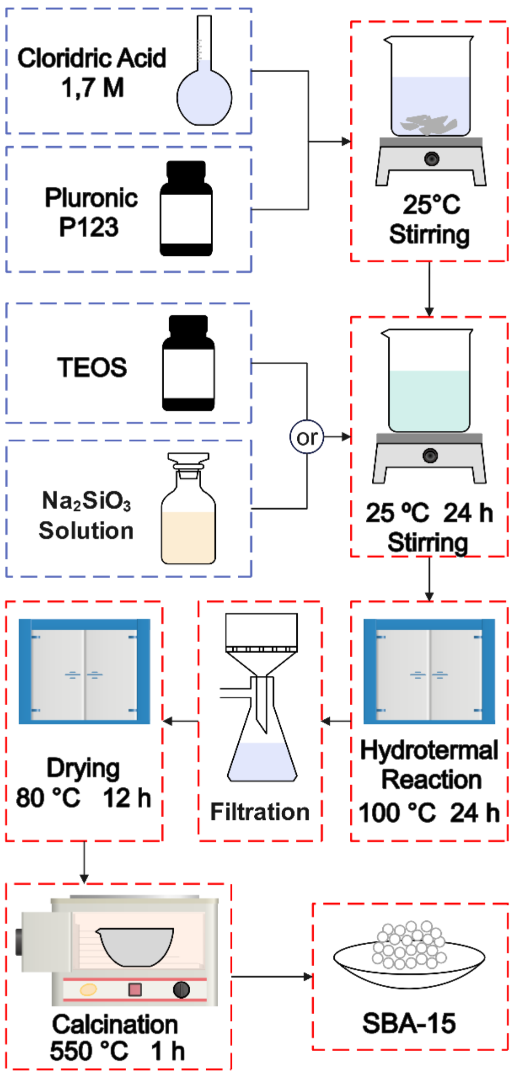

Fig. 1. SBA-15 synthesis procedure.

3. Results

RHA presented a chemical composition of 84.76% SiO_2, confirming its potential for application as a raw material silicon source. The Na_2SiO_3 obtained presented a composition of 7.41% Na_2O and 16.52% SiO_2, with recovery of 54.21% of the silicon present in the raw ash.

The majority chemical composition and determination of the loss-on-ignition (LOI) content of the SBA-15 samples obtained are presented in Table 2.

Table 2. Major chemical composition of the synthesized SBA-15 samples.

Sample	SiO_2 (%)	Other Elements (%)	LOI (%)
TEOS	94,35	0,35	5,30
Na_2SiO_3-3	93,39	0,04	6,57
Na_2SiO_3-9	93,02	0,05	6,93
Na_2SiO_3-11	91,84	0,02	8,14

The SBA-15 chemical composition confirm the structure of the material based mainly on silicon (>90% in all samples), and the results using sodium silicate were very similar to those obtained for the material synthesized with TEOS. Furthermore, the low LOI (<8%) indicates that the calcined material was achieved after the good removal of the used template, which should make its pores more available for application as a support.

The good quality of the synthesized material is in Table 3, where the textural properties are presented. All materials obtained are mesoporous (diameter between 20 – 500 Å) and with good pore volume and specific surface area. The good quality of the material synthesized with sodium silicate is observed in relation to that using TEOS [7].

Table 3. Textural properties of SBA-15 samples.

Sample	Specific Surface Area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
TEOS	777.14	0.86	44.10
Na_2SiO_3-3	577.25	0.81	56.00
Na_2SiO_3-9	501.56	0.85	67.55
Na_2SiO_3-11	516.17	0.86	66.77

These results serve to demonstrate that reducing the aging time (sample Na_2SiO_3-9) and carrying out aging in static condition (sample Na_2SiO_3-11) do not compromise the quality of the material obtained.

Furthermore, other authors such as Henao et al. [7] obtained mesoporous silicas SBA-15 type with 604 cm^2/g, 1,192 cm^3/g and 76 Å, results very similar to those obtained in the work and confirming its quality.

Figure 2 presents the FTIR results of the synthesized mesoporous silicas, where the characteristic peaks of silica, siloxane (*Si-O-Si*) - 1060 cm^{-1}, can be visualized. As well as the stretching bands (*Si-OH*) - 970 cm^{-1} of the silanol group and the symmetric stretching of the *Si-O-Si* bond - 800 cm^{-1}, commonly seen in mesoporous silicas such as SBA-15 [7,14].

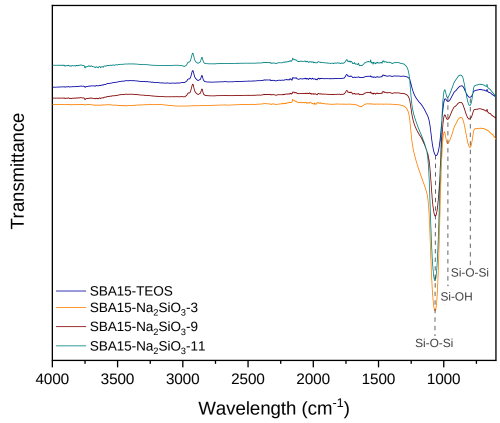

Fig. 2. FTIR results of the synthesized SBA-15.

Finally, the adsorption capacity results are presented in Table 4. As expected, despite the good textural properties, SBA-15 does not present a good CO_2 adsorption capacity by itself. All results were less than 0.11 mmol/g, including the silica synthesized with TEOS and also that synthesized by the authors Henao et al. [7].

Table 4. CO_2 Adsorption Capacity results.

Sample	CO_2 Adsorption Capacity (mmol/g)	Reference
TEOS	0.03	This work
Na_2SiO_3-3	0,00	This wok
Na_2SiO_3-9	0.00	This wok
Na_2SiO_3-11	0.05	This wok
SBA-15	0.11	[7]
SBA-15-60PEI	1.13	[7]
Na_2SiO_3-3-60TEPA	1.70	This wok

However, after amine PEI type impregnation, the same authors increased the capacity to 1.13 mmol/g, a very satisfactory result from an application point of view.

In a preliminary test, the silica obtained by test Na_2SiO_3-3 was impregnated with 60% TEPA obtained a capacity of 1.70 mmol/g. This is a very satisfactory result and which indicates its potential of this synthesized materials as a support for amine impregnation. Other tests will be carried out using 400 ppm of CO2 concentration in the presence and absence of moisture in the focus of the direct air capture process that Repsol Sinopec Brasil is implementing.

4. Conclusion

Good quality sodium silicate can be obtained from rice husk ash, and can be used for the synthesis of porous support. The quality of the synthesized SBA-15 samples was confirmed through their main chemical characterizations and textural properties.

Furthermore, preliminary testing confirms that with the incorporation of amines, the material presents itself as an excellent adsorbent for capturing CO_2.

In addition to the need for continued testing and an economic evaluation of the process, the use of waste to develop a high-performance adsorbent is very interesting from an economic and environmental point of view.

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