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# REVALUING GLASS POWDER RESIDUES: SYNTHESIS OF A HIGH SILICA ZSM-5 USING HYDROFLUORIC ACID.

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RESUMO: ZSM-5 com alto conteúdo em silício foi obtida com êxito a partir de resíduo de pó de vidro. A fonte de sílica foi usada após o pré-processamento com ácido clorídrico e como foi fornecido. A síntese foi realizada seguindo a rota do flúor usando hidróxido de tetrapropilamônio como direcionador de estrutura orgânico. Os produtos foram analisados mediante difração de raios x e microscopia eletrônica de varredura. Os resultados foram comparáveis com os publicados de silicalita-1 sintetizada com tetraetil ortosilicato.

PALAVRAS-CHAVE: resíduo de pó de vidro; zeólita tipo MFI; ácido fluorídrico.

ABSTRACT: A high sílica ZSM-5 was successfully obtained from glass powder residues. The silica source was employed after previous treatment with hydrochloric acid and as provided. Synthesis was performed following the fluoride route using tetrapropylammonium hydroxide as organic structure-directing agent. Products were analyzed by x-ray diffraction and scanning electron microscopy. Results were comparable with the ones published of silicalite-1 obtained from tetraethyl orthosilicate.

KEYWORDS: glass powder residue; MFI type zeolite; hydrofluoric acid.

## 1. INTRODUCTION.

Production of undesired industrial residues has increased during last decades (Hoornweg et al, 2013) and new methods of recycling and revalorization are being searched (Venancio et al, 2010).

Zeolites are crystalline tectosilicates constituted by ($SiO_4$) and ($AlO_4$) tetrahedra connected through the O atoms of their vertices (Payra and Dutta, 2003). These materials have a wide range of applications including catalyses and adsorption (Camblor and Hong, 2011).

ZSM-5 is a well-known MFI type zeolite (Olson et al, 1980). Silicalite-1 is a pure silica ZSM-5 and was firstly synthesized by Flanigen et al in 1978 (1978, a). It is characterized by its hydrophobicity and its adsorption properties (Flanigen et al, 1978, b). Due to this fact, the applications of this zeolite are currently studied. As an example, silicalite adsorption of $CO_2$, which is a well-known green-house gas, and $N_2$ was investigated by Kennedy and Tenzel (2013).

Production of zeolites like silicalite-1 is expensive due to the need of pure reagents and the energetical costs. So, the aim of this research project is to study the possibility of using industrial residues as a silica source in the synthesis of a high silica ZSM-5. Glass powder residues have been chosen due to their impossibility to be incorporated in the usual recycling process (Muñoz et al, 2000).

## 2. MATERIALS AND METHODS.

Reagents employed in this work were glass powder residues provided by a company in Rio Grande do Norte (Brazil) that makes colourless glass, HCl (37%, Proquimios), TPAOH (1M in water, Sigma Aldrich), HF (40% in weight, Cinética) and deionised water.

Starting with the Si concentration process (Alves et al, 2013), residues were macerated and treated with 250mL of a 0.1M HCl solution for 6h in continuous agitation. Afterwards, they were washed repeatedly with deionised water and dried. This process was performed twice. The composition of the samples was quantified by energy dispersive X-ray analysis (EDX, Shimadzu model EDX-720).

High silica ZSM-5 was synthesized using as silica source three different samples of glass powder residues: as provided, and treated in HCl once and twice. The synthesis procedure is based on the one described by Flanigen et al (1978, a, b). The synthesis gel composition was $SiO_2$: 0.5 TPAOH: 0.5 HF: 40 $H_2O$. Firstly, the chosen sample, TPAOH and deionised water were stirred for 2h. Then, HF was added and the resulting mixture was stirred for 30 minutes. The gel was transferred to a TEFLON autoclave and then, into a stainless steel autoclave. Finally, it was placed inside a static oven at 180ºC for 10 days. The resulting products were filtered, washed with deionised water, dried and characterized by x-ray diffraction (XRD, Siemens model D5000 diffractometer) and scanning electron microscopy (SEM, Hitachi TM3000).

## 3. RESULTS AND DISCUSSION.

The chemical composition of the silica source samples before and after the HCl treatment is shown in Table 1. The purity of silica increased from approximately 76% to nearly 92%. Yields of each step were calculated and resulted in 72.2% (first HCl treatment) and 81.2% (second HCl treatment) respectively, and the total yield of the whole process was 58.6%. This last value is low enough to considerate only performing the first cleaning step. But to make a good evaluation, the synthetic process will continue with the three samples described.

**Table 1.** Glass powder residues composition as provided and after HCl treatments.

| **Sample** | **P01** | **P02** | **P03** |
|---|---|---|---|
| Treatment | As provided | 1x HCl | 2x HCl |
| $SiO_2$ (%) | 76.288 | 80.502 | 91.582 |
| CaO (%) | 21.624 | 17.737 | 7.001 |
| $SO_3$ (%) | 1.372 | 1.041 | 1.090 |
| $Fe_2O_3$ (%) | 0.383 | 0.320 | 0.284 |
| Others (%) | 0.333 | 0.400 | 0.043 |

Synthesis of high silica ZSM-5 was achieved in fluoride media after 10 days with the three samples mentioned above. In all cases the resulting product was a pulverulent brownish solid. Yields were calculated employing the weight of the final dried products and they resulted 75.5%, 63.0% and 67.8% respectively.

All the samples were characterized by scanning electron microscopy (SEM), presented in Figure 1. Morphology of the samples was elongated prisms.

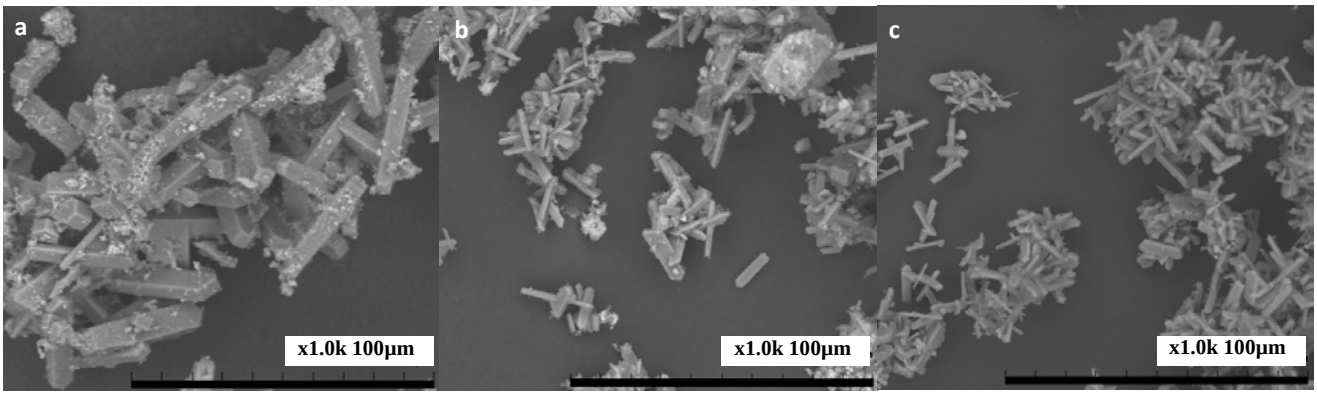


**Figure 1.** SEM images from the zeolite products P01Z01 (a), P02Z01 (b) and P03Z01 (c).

As it can be seen in the samples with a poorer silica source, crystals were covered by a kind of contamination whose provenance was the starting reagent. A preliminary EDX analysis of these contaminations was performed in each sample and it showed that probably a high proportion of the impurity of the silica source was concentrated in this. This technique was also applied to analyse some of the crystals and showed that they were mainly composed by Si.

X-ray diffraction was also employed to characterize the samples and are shown in Figure 2. They were compared with the XRD of MFI structure provided by the IZA Structure Database (International Zeolite Association) showing the same diffraction pattern. Peaks of each sample XRD coincide with that of TPA-ZSM-5, whose symmetry is orthorhombic, space group Pnma (Baerlocher and McCusker).

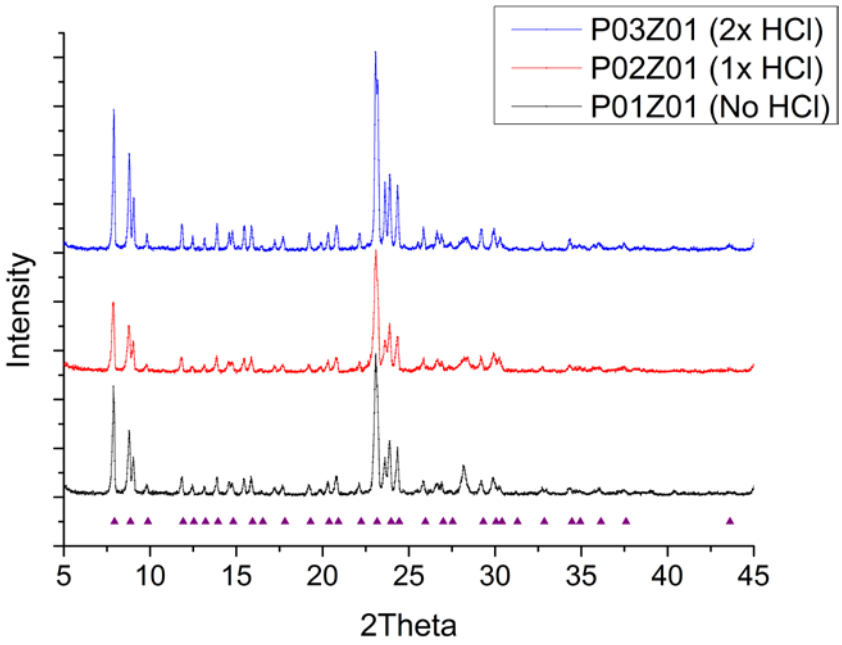


**Figure 2.** X-ray diffraction patterns of the zeolite samples obtained from the powder glass residues. Main TPA-ZSM-5 peaks are marked with purple triangles.

The relative crystallinity of the samples was calculated following the ASTM procedure D 5758-01 (American Society for Testing and Material, 2002). Results are presented in Table 2. The sample whose silica source had a higher Si percentage resulted in the most crystalline product of the three obtained. The other two had similar relative crystallinity and notably lower values compared with the most crystalline sample. The most probable reason of this descent in crystallinity would be the contamination discovered in the SEM micrographs.

**Table 2.** Relative crystallinity of the silicalite samples.

| Sample | P01Z01 | P02Z01 | P03Z01 |
|---|---|---|---|
| Treatment | As provided | 1x HCl | 2x HCl |
| Crystallinity Integrated Peak Area | 86.53% | 82.01 % | 100 % |

## 4. CONCLUSIONS

In this work, a Si concentration process was successfully performed with glass powder residues. EDX showed that a maximum of approximately 92% was achieved in the most concentrated solid. A high silica ZSM-5 from these Si source samples was synthesized following the fluoride route.

Resulting products were observed by SEM and consisted on elongated prisms. The ones synthesized from the less pure Si source were covered by contamination, which is mostly composed by the impurity materials observed in the initial reagent (preliminary data).

X-Ray diffractograms were also studied and showed the coincidence with the MFI structure provided by the IZA Database. The relative crystallinity of the samples increased for the most pure starting product.

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