Synthesis and Characterization of Microporous/Mesoporous SAPO-5

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***Abstract*—Proposals have appeared aiming at the removal of sulfur in fuels by means of adsorption processes. The molecular sieves, silicoaluminiumphosphates, type SAPO, have been presented as an excellent adsorbent, with a great thermal and hydrothermal stability, and the impregnation of metal have became the adsorption even more selective, as they are a crystalline microporous material, and its acidity reaches intermediate values between the zeolite and aluminophosphate (ALPO's). Therefore, researchers have been dedicated to synthesize mesoporous SAPO-5. This work aims to synthesize and characterize the Microporous (SAPO-5) and mesoporous (SAPO-5M) with the addition of specific template (TPOD), supported with different levels of transition metals, Ni and/or Zn. Thus, were synthesized the SAPO-5 and the SAPO-5M by hydrothermal method. Characterization techniques such as X-ray diffraction (XRD) and Textural Analysis (N2 adsorption/desorption) were carried out. The results are promising since the material had a surface area increase of 195.2 m^2 g^{-1} to 229.8 m^2 g^{-1}, about 19%, and the BET area an increase of five times in the pore diameter, with the addition of the reagent to obtain higher porosity. It follows that the process of synthesis of SAPO-5 and SAPO-5M shows to be effective for increasing the area and pore volume and with this addition of the reagent to obtain the mesoporosity, did not alter the crystallinity nor the structure of the material.**

***Index Terms*—Silicoaluminiumphosphates; X-ray diffraction ; Mesoporous.**

I. INTRODUCTION

X-ray diffraction is a successful method for identifying ordered phases. The X-rays are produced by electron bombardment of a cathode, accelerated by high voltage (20-50 kV), exciting the innermost electrons. By focusing a beam of X-rays in a crystalline material, it interacts with atoms present, yielding the diffraction phenomenon.

The SAPO-5 shows a characteristic pattern of X-ray diffraction, which may be used qualitatively to identify the material and detecting the existence of other crystalline and quantitatively ways to determine the purity and / or crystallinity (Giannetto, 1989).

Figure 1 shows the standard x-ray pattern for SAPO-5 material.

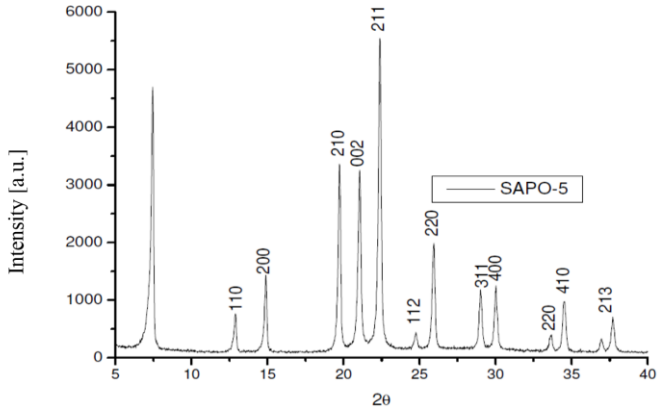


Figure 1 - X-ray pattern of the sample of SAPO-5.

Source: IZA-SC (http://topaz.ethz.ch/IZA-SC/PDFfiles.htm).

The X-ray pattern of SAPO-5, illustrated in Figure 1, show the characteristic peaks for this material. It is observed that the main peaks with higher intensity, showing larger crystallites and thus higher crystallinity. On the other hand the absence of no characteristic peaks indicates an amorphous material with disordered structure (RABELLO, 2005). The uniform pore size defined by the crystal structure enables the use of these materials for separation processes and as adsorbents for the adsorption of contaminants in fuels.

This paper aims to synthesize and characterize SAPO-5 microporous and mesoporous SAPO-5, in which the mesoporous material was obtained by adding the 3-[(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride (TPOD) reagent.

II. MATERIALS AND METHODS

The microporous SAPO-5 synthesis was performed using the two-phase medium, as described by Urbina (1997) adapted by Cabral (2008). The mesoporous sapo-5 was synthesized using the methodology described by Danilina *et al.* (2010) Danilina *et al.* (2011), replacing the template TPHAC (3-[(trimethoxysilyl)propyl]hexadecyl-dimethylammonium chloride) by TPOD. The impregnation was made by aqueous process using zinc chloride ($ZnCl_2$) and nickel nitrate hexahydrate ($NiNO_3$ $6.H_2O$), after impregnating the support were calcined in the following proportions: NiO and ZnO: 1% Ni / SAPO-5; 0.75% Ni 0.25% Zn / SAPO-5; 0.50% Ni 0.50% Z.n / SAPO-5; 0.75% Ni 0.25% Zn / SAPO-5; 1% Zn / SAPO-5

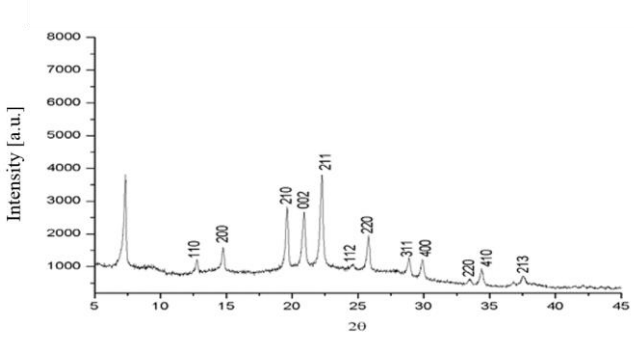
The analyzes were performed using the diffractometers Shimadzu, model XRD 6000 (LCM) and model XRD 7000 with Cu Kα radiation source (λ = 1.54 nm), obtained by 40 kV filament current of 30 mA. The measurements were performed at a rate 2° min^{-1}. The data were obtained at 2θ scan range from 5 to 45 degrees.

Textural analysis: The BET method was used through the N_2 adsorption at liquid N_2 temperature (-196°C). The isotherms of calcined adsorbents were obtained by equipment Quantachrome Nova 1200e. For this, about 0.21 g of the sample was pretreated at 300°C for 3 hours, under vacuum, to then be subjected to nitrogen adsorption at -196°C.

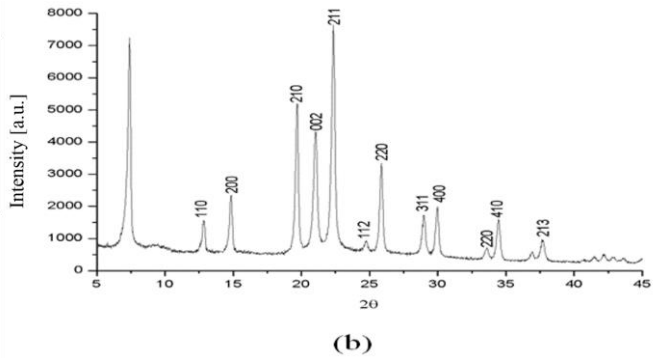
III. RESULTS AND DISCUSSION

Figures 2a-b shows the X-ray pattern for the SAPO-5 non-calcined and calcined support. It was confirmed that the synthesis was effective for the substrate and it was found that calcination does not compromise the structure of the delimited by rings of 12 tetrahedral pores, unlike, there has been an increase in crystallinity that increases the intensity of the diffraction peaks (Figure 2b) for the calcined material (without organic template), proving the good thermal stability of the material and better structural ordering after removing the template. This behavior was also observed by MacIntosh and Huang (2013), Tang et al. (2013), Zhao et al. (2012)

Figure 2 - X-ray pattern of the support SAPO-5 (a) uncalcined and (b) calcined.



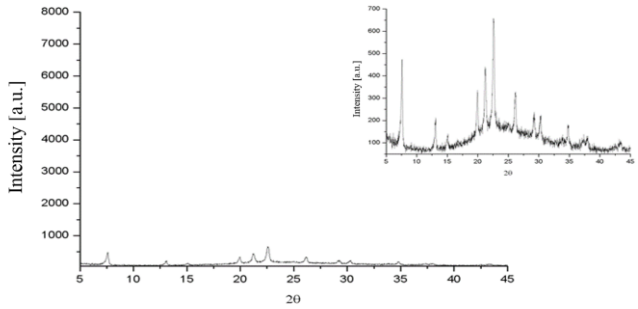
(a)



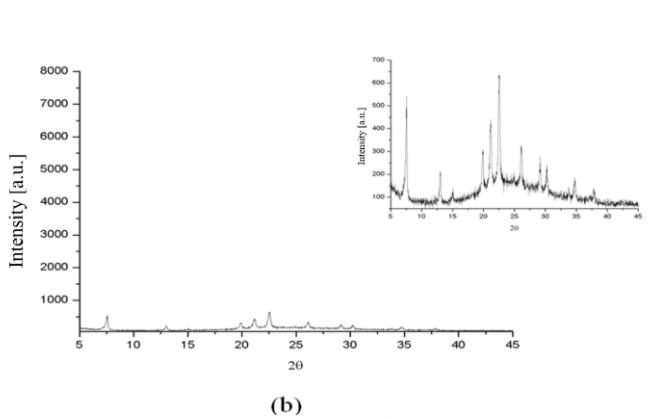
(b)

In Figures 3a-e X-ray pattern for microporous adsorbent materials (SAPO-5) impregnated with different metal contents (Zn/Cu) are presented. After impregnating the calcined support with the adsorbent, was observed by means of Figures 3a-e the reduction of approximately 90% in relation to the support, the intensities of the diffraction peaks, causing a disarrangement of the crystalline structure featuring a material of low crystallinity, identified by the elevation of the baseline for this materials. This outstanding reduction could be related to the incorporation of the adsorbents oxides supported metal which may be deposited in the pores of the support.

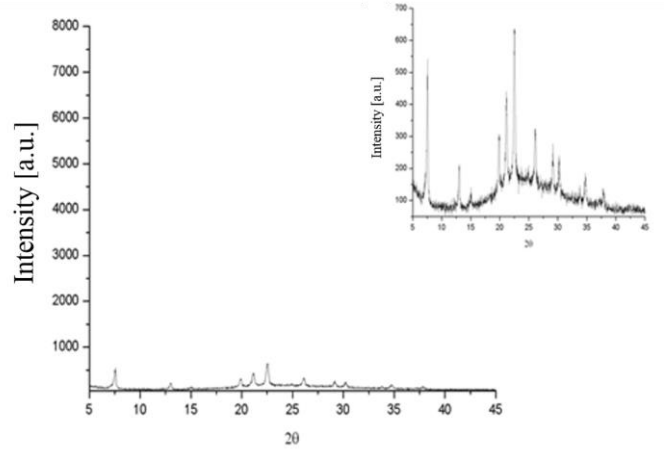
Figure 3 - X-ray pattern of the adsorbents (a) 1% Ni / SAPO-5; (b) 0.75% 0.25% Ni Zn / SAPO-5; (c) 0.50% 0.50% Ni Zn / SAPO-5; (d) 0.75% 0.25% Ni Zn / SAPO-5; (e) 1% Zn / SAPO-5, with their real scales and changes on the focal length of the curve.



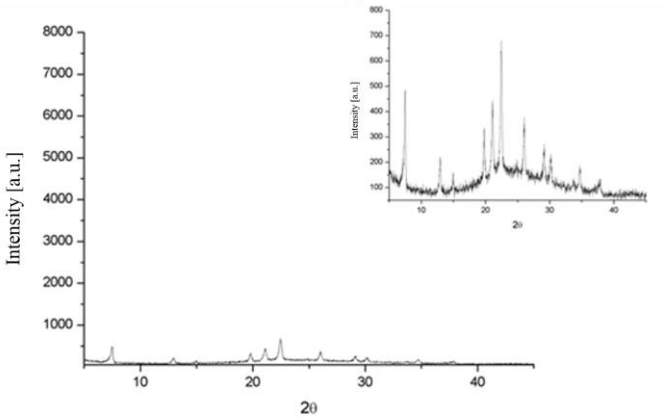
(a)



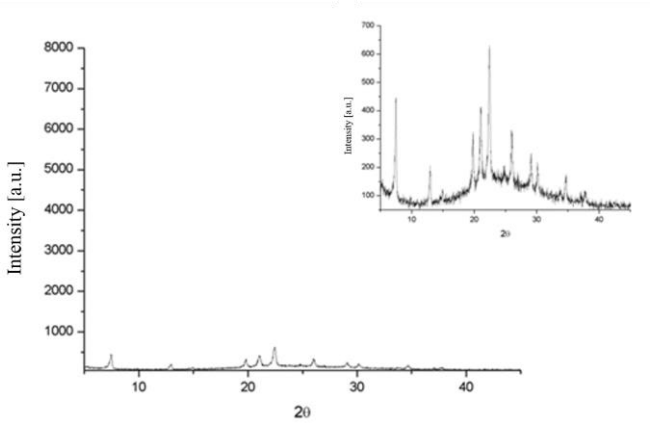
(b)



(c)



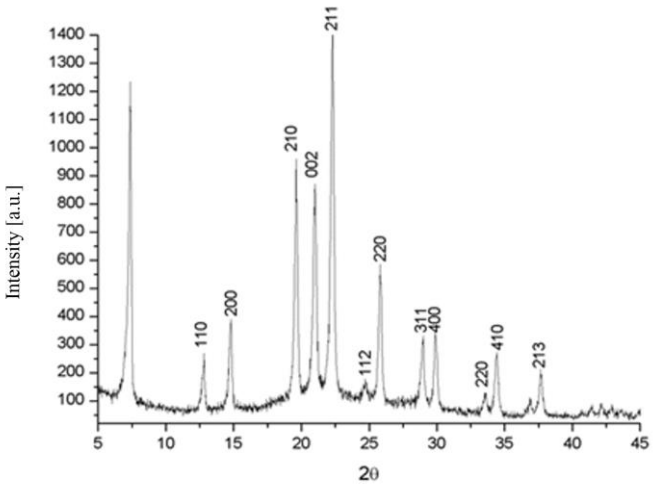
(d)



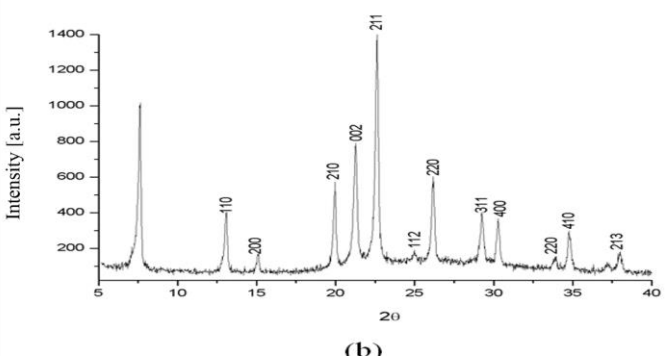
(e)

Figures 4a-b shows the results from XRD for the SAPO-5M (mesoporous) calcined and non-calcined. Can be seen that the crystalline phase AFI was successfully obtained as diffraction patterns of literature. It is observed that, according to Figures 4a and 4b, the relative intensity of the diffraction planes of uncalcined and calcined material was almost the same with intensity about 1400, indicating that the addition of the reagent TPOD did not affect the crystallinity of mesoporous support with respect to microporous.

Figure 4 - X-Ray pattern of SAPO-5M support (a) uncalcined and (b) calcined.



(a)



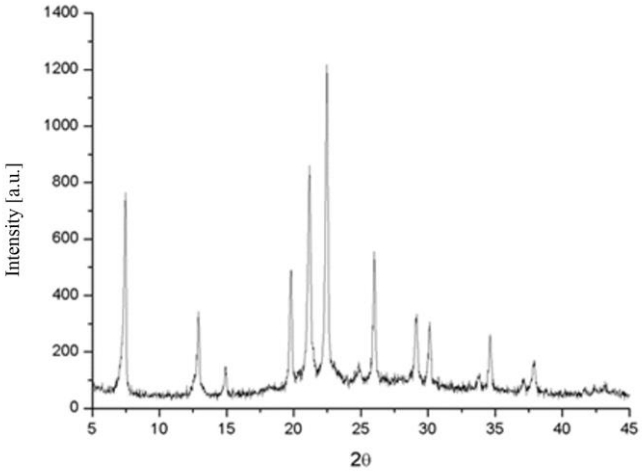
(b)

As opposed to the adsorbents with microporous support, the ones supported in mesoporous materials had good crystallinity with defined peaks characteristic of AFI phase.

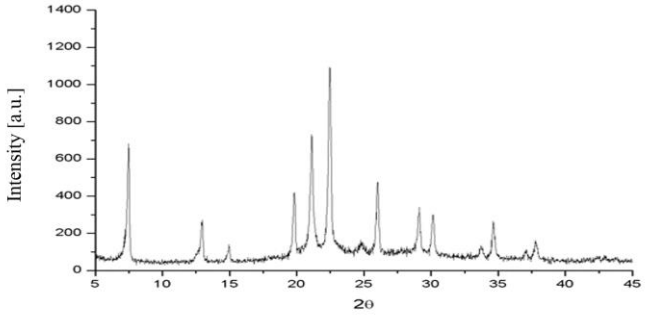
It can be observed for the SAPO-5M that it was possible to impregnate the various oxides, causing no significative disorder in the material, compared with the SAPO-5. The curves of diffraction X-rays are plotted in Figures 5a-5e for adsorbents: 1% Ni / SAPO-5M; 0.75% Ni 0.25% Zn / SAPO-5M; 0.50% Ni 0.50% Zn / SAPO-5M; 0.75% Ni 0.25% Zn / SAPO-5M; 1% Zn / SAPO-5M, with the addition of the reagent TPOD.

In Figures 5a-e, curves X-ray diffraction for the mesoporous adsorbent materials (SAPO-5M) impregnated with different concentrations of metals (Zn/Cu) are presented.

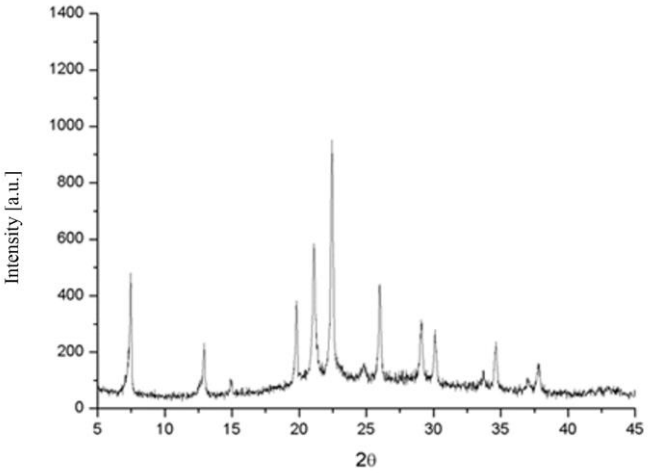
Figure 5 - X-Ray pattern for adsorbents (a) 1% Ni / SAPO-5M; (b) 0.75% 0.25% Ni Zn / SAPO-5M; (c) 0.50% 0.50% Ni Zn / SAPO-5M; (d) 0.25% 0.75% Ni Zn / SAPO-5M; (e) 1% Zn / SAPO-5M.



(a)



(b)



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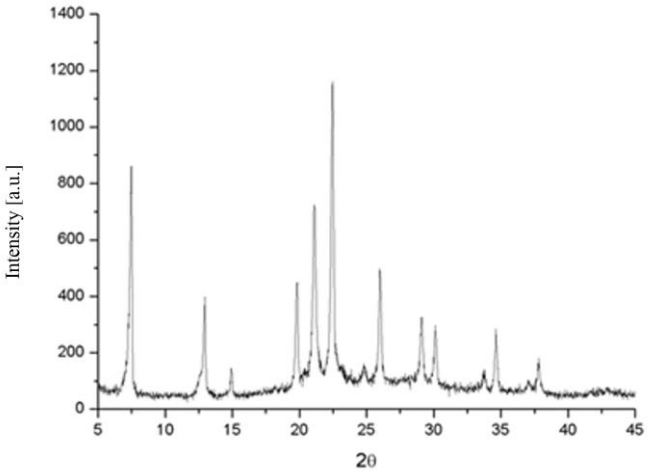

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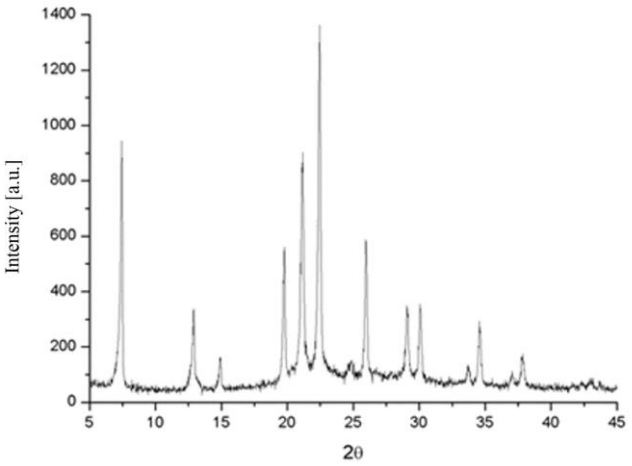

(e)

Can be noted that the characteristic peaks of the adsorbent material and impregnated with 1% metal (Ni or Zn) and 0.25% Ni 0.75% Zn / SAPO-5M had the highest intensity (approximately 1200).

It is noteworthy that different from what occurred with the microporous materials, impregnating the mesoporous support not significantly reduced the intensity curves of X-ray diffraction, and a diagnosis in that metal oxides impregnated in mesoporous materials did not cause the covering of the support lens, that is the oxides are dispersed on a mesoporous support.

In Table 1 the results for textural analysis (BET) of the supports and adsorbents with different levels of metals are presented.

Table 1 - Results obtained by N_2 adsorption/desorption for SAPO-5 and SAPO-5M supports and adsorbents.

Samples	BET ($m^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Pore diameter (Å)
SAPO-5	-	0,269	7,011
1% Ni/SAPO-5	-	0,246	7,021
0,75Ni 0,25% Zn/SAPO-5	-	0,180	7,207
0,50Ni 0,50% Zn/SAPO-5	-	0,231	7,069
0,25Ni 0,75% Zn/SAPO-5	-	0,231	7,078
1% Zn/SAPO-5	-	0,249	6,999
SAPO-5M	229,8	0,090	-
1% Ni/SAPO-5M	136,0	0,077	22,693
0,75Ni 0,25% Zn/SAPO-5M	122,8	0,108	35,369
0,50Ni 0,50% Zn/SAPO-5M	137,1	0,099	28,867
0,25Ni 0,75% Zn/SAPO-5M	181,3	0,139	30,791
1% Zn/SAPO-5M	138,3	0,117	34,056

According to Table 1, the addition of reagent TPOD caused the pore diameter to increase four times the microporous SAPO-5. It is noteworthy that these increases in pore diameters are interesting to the adsorption process, since the larger the diameter, the more bulky molecules can be adsorbed mainly the sulfur compounds found in gasoline, for example, thiophenes. Thus, this study was able to achieve the goal, since greatly increased the pore diameter.

IV. CONCLUSION

It is noteworthy that different from what occurred with the microporous materials, impregnating the mesoporous support not significantly reduced the intensity curves of X-ray pattern, and a diagnosis in that metal oxides impregnated in mesoporous materials did not cause the covering of the crystalline supports. That is, the oxides are dispersed on a mesoporous support. The synthesis of these materials was performed with complete success. Formed a highly crystalline material, free of amorphous phase, and obtained AFI phase, particularly adsorbents and SAPO-5 and SAPO-5M media, since for SAPO-5 adsorbents impregnated with metals desired phase was disorganization structural.

V. ACKNOWLEDGEMENTS

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