

## Synthesis of Ni-Pt catalysts and characterization

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**Keywords:** Zeolite MCM-22, Pt-Ni/MCM-22, ion exchange.

**Abstract.** In this work, bifunctional catalysts using the MCM-22 zeolite as support and the nickel and platinum metal as hydrogenation/dehydrogenation sites were prepared. The method used for metal dispersion on the zeolite was the competitive ion exchange, using the amine complex  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  and  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ . After the exchange reactions, the samples were calcinated at 500° C for 2 hours and reduced at this same temperature under hydrogen flow. The MCM-22 zeolite and samples containing the metal were characterized by the techniques of: EDX, XRD, DTA/TGA. The diffractions of the precursor MCM-22 (P) presented typical peaks of the MWW topology composed by intercalated lamellar layers with organic molecules that are constituents of the template (HMI). According to the XRD pattern of the calcinated sample, no peaks related to the organic material which is responsible to produce the MCM-22 zeolite were detected. By thermogravimetry it was verified that the removal of the template took place between 500 and 650 °C proving the effectiveness of the removal process. The chemical analysis by X ray espectralometric was evidenced this the incorporation in the zeolites of platinum and nickel for all the texts in study. Results from XRD confirming the stability and crystal in study of zeolites.

### Introduction

The activity of bifunctional catalysts with transition metal and supported on zeolites showed good activity in the isomerization reaction. Such metals introduced into the zeolite by ion exchange competitive show is an important and attractive route for isomerization of n-paraffin and the insertion of a second metal bifunctional catalysts leads to the attainment of different solid properties of those containing only one metal. In the case of the isomerization catalyst used in replacing monometallic platinum catalysts currently used, expensive, for a bimetallic catalyst Pt-Ni would make the process cost minimized [1, 2].

The MCM-22 zeolite was originally synthesized by Mobil researchers in 1990 [3]. This ion exchange aims to obtain a catalyst containing metal atoms attached to or located in the zeolite structure [4]. The ion-exchange method competitive to a more homogeneous distribution and better dispersion of metals in the zeolite as compared to the conventional ion exchange. This method consists of introducing in the liquid phase (solution of zeolite) a large excess of competitive ions ( $\text{NH}_4^+$ ) with the desired metal ions [5].

This study aimed to produce the type of zeolite MCM-22 through the static method and develop catalysts (platinum-nickel supported on zeolite MCM-22 (Pt-Ni/MCM-22)). These catalysts were obtained by competitive ion exchange using aqueous solution of complex of platinum and nickel, which were prepared Pt/MCM-22, Ni/MCM-22 and Pt-Ni/MCM-22.

## Experimental

Followed the procedure described by [6]. The procedure used for the dispersion of metals in the zeolite was ion exchange competitive is to add slowly the solution of the complex cation  $[\text{Pt}(\text{NH}_3)_4]^{+2}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{+2}$  and  $\text{NH}_4^+$  ions in the solution on the suspension at room temperature. After the exchange, the solution remained stirring for 1h. Then the solid was centrifuged and washed with deionized water to remove the chloride ions. The solids were subjected to the drying oven at a temperature of 80 ° C/24h. Finally the solids were calcined following the following steps:

Step I: consisted of heating the sample under continuous flow of nitrogen at a flow rate of 100 mL/g<sub>cat</sub>.min, from ambient temperature to 200 °C with a heating ramp of 10 °C/min., kept at this temperature for 60 min.

Step II was carried out by heating under the flow of synthetic air with a heating ramp of 2 °C/min, 200 °C até 450 °C, kept at this temperature for 120 min.

## Characterizations

### Chemical analysis by the spectrometer X ray energy dispersive (EDX)

The equipment used was a spectrometer for X ray Energy Dispersive - EDX-700 Shimadzu. The analysis parameters are shown in Table 1.

Table 1. Conditions for analysis by EDX

Method	Qual-Quant
Atmosphere:	He
Channels:	Na-Sc, Ti-U
Sample:	Powder
Form of Results:	Element

### X ray diffraction (XRD)

We used the powder method was studied using a Shimadzu diffractometer XRD-6000 with CuK $\alpha$  radiation, voltage 40 KV, 30 mA, step size of 0.020 2 $\theta$  and time per step of 1.000 s, scan rate of 2°(2 $\theta$ )/min with 2 $\theta$  angle covered from 3 to 50°.

### Thermogravimetric analysis (DTA/TGA)

For testing we used a thermogravimetric, Thermogravimetric Analyzer TGA-51 Shimadzu coupled to a computer monitored by the software TA-60 WAS Collection Monitor. The samples were analyzed in the temperature range 30-100 °C in a heating rate of 10 °C/min and a flow rate of 50 mL/min, under air.

## Results and Discussion

### Chemical analysis by the spectrometer X ray energy dispersive (EDX)

Table 2 presents the results of chemical analysis of the precursor material MCM-22 (P) and zeolite Na-MCM-22 and mono and bimetallic catalysts containing platinum and nickel.

Table 2. Chemical composition of parent material MCM-22 (P), zeolite Na-MCM-22 and catalyst Pt/MCM-22, Ni/MCM-22 and Pt-Ni/MCM-22.

Samples	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	PtO <sub>2</sub> (%)	NiO (%)	Impurities (%)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>
Precursor MCM-22 (P)	91,646	7,936	--	--	0,418	11,55
Zeolite MCM-22	91,557	8,061	--	--	0,383	11,36
Pt/MCM-22	91,128	8,066	0,664	--	0,142	11,30
Ni/MCM-22	90,978	8,526	--	0,310	0,187	10,67
Pt-Ni/MCM-22	90,228	8,417	1,008	0,153	0,194	10,71

From the data presented in Table 2 can confirm that both the precursor materials as the zeolitic materials showed high concentration of silica (SiO<sub>2</sub>) and low alumina (Al<sub>2</sub>O<sub>3</sub>) in the zeolite structure, which gives them a reason SiO<sub>2</sub>/AlO<sub>3</sub> characteristic MWW structure [7].

You can see in Table 2, which after calcination was a small reduction SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> reason for zeolite Na-MCM-22 that reason remained almost constant. This fact is in agreement with the literature [8].

After the process of competitive ion exchange of platinum and nickel in the MCM-22, it is their presence through the content of the oxides of platinum (PtO<sub>2</sub>) and nickel (NiO) in the sample. You can see that the percentage of impurities in the catalysts were lower when compared with the precursor and the zeolite, resulting in a purer material.

### X ray diffraction (XRD)

Figs. 1 and 2 show the diffraction of X rays regarding the samples as progenitor (MCM-22 (P)) and as sodium (Na-MCM-22).

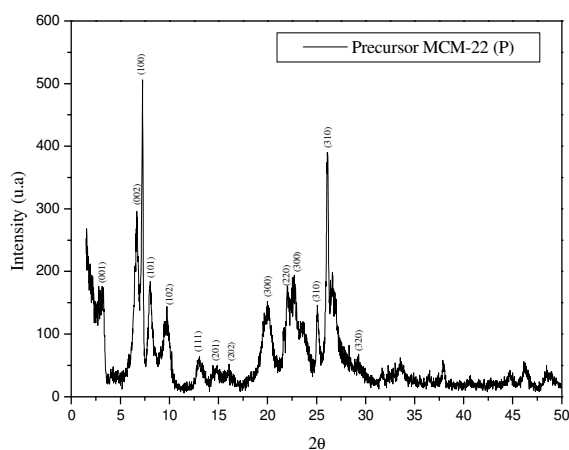


Fig. 1. Diffractogram of the precursor MCM-22(P)

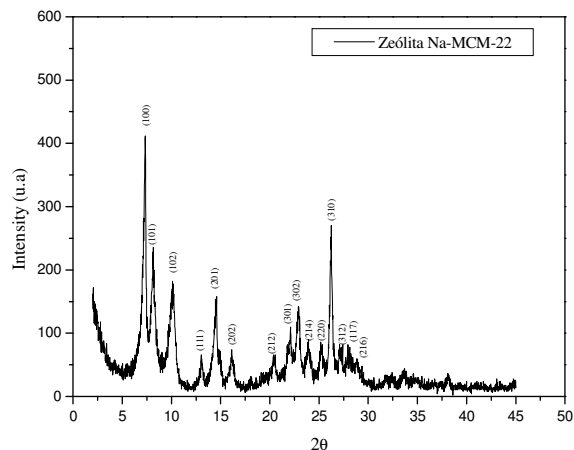


Fig. 2. Diffractogram of zeolite Na-MCM-22

From the XRD pattern of parent MCM-22 (P), we can observe the peaks indexed as (001) and (002) that is characteristic of the MWW topology. The same is located in the precursor material at:  $2\theta = 6.68^\circ$  (MCM-22 (P)). Topology MWW precursors present in MCM-22 (P)

corresponds to a lamellar structure consisting of lamellae of 2.5 nm interspersed with molecules of the HMI [10, 11].

According to Pergher et al., (2003), calcination of the precursor MCM-22 (P), resulted in the disappearance of the peaks indexed as (001) and (002), which overlaps resulting in zeolite Na-MCM-22 shown in Fig. 2.

Figs. 3, 4 and 5 show XRD patterns of X rays regarding the catalysts Pt/MCM-22, Ni/MCM-22 and Pt-Ni/MCM-22 respectively.

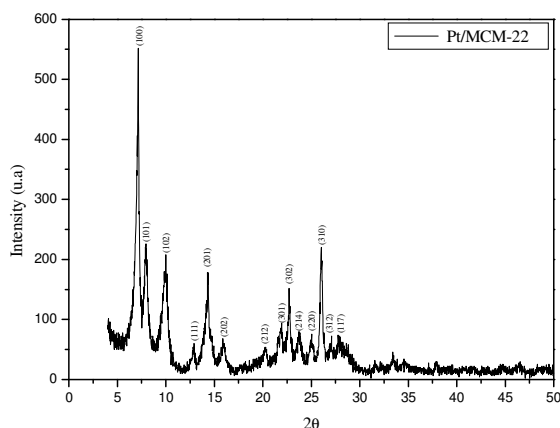


Fig. 3. Diffractogram of the catalyst Pt/MCM-22

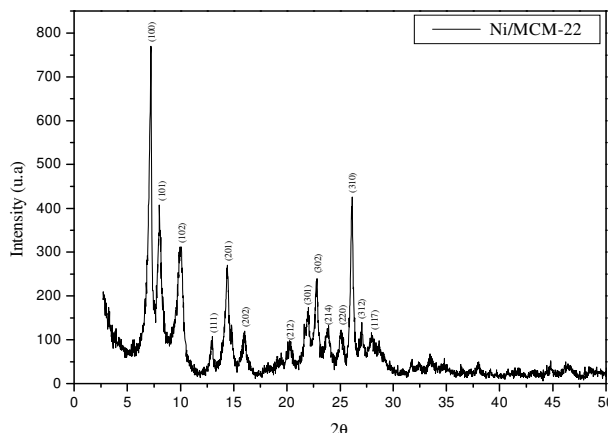


Fig.4. Diffractogram of the catalyst Ni/MCM-22

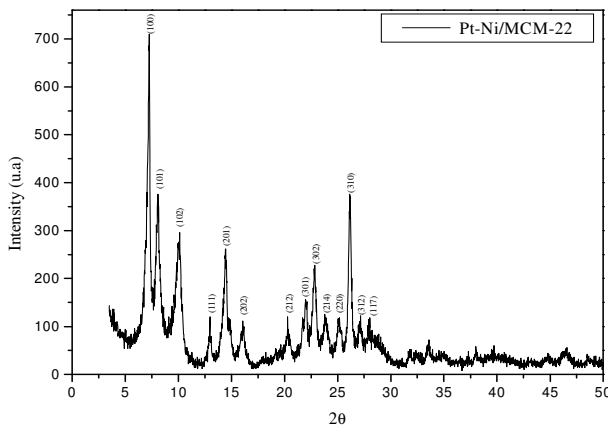


Fig. 4. Diffractogram of the catalyst Pt-Ni/MCM-22

Comparing the XRD patterns of catalysts after ion exchange and calcination process (Figs. 3, 4 and 5 respectively) with the XRD pattern of zeolite Na-MCM-22 (Fig. 2) was also observed that the peaks remain almost intact.

Table 3 presents the crystallographic parameters (lattice parameters and unit cell volume) of different samples obtained by diffraction of X rays.

Table 3. Results of crystallographic parameters calculated by the diffraction of X rays

Amostras	Parâmetros de rede (nm)			Volume da cela unitária (nm) <sup>3</sup>
	<b>a</b>	<b>b</b>	<b>c</b>	
MCM-22 (P)	1,4210	1,4210	2,6464	4,6277
Na-MCM-22	1,4180	1,4180	2,4970	4,3480
Pt/MCM-22	1,4231	1,4231	2,4953	4,3761
Ni/MCM-22	1,4202	1,4202	2,3995	4,1909
Pt-Ni/MCM-22	1,4164	1,4164	2,5664	4,4584

You can see from the data in Table 3 that the crystallographic parameters of samples MCM-22 (P) and Na-MCM-22, and the samples after ion exchange followed by calcination did not show marked changes in values. These small changes are due to the fact that metals are incorporated in nano-quantities, ie, consist of very small particles that do not significantly change the structure of the zeolite.

### Thermogravimetric analysis (DTA/TGA)

The curves of thermogravimetric analysis for the parent material MCM-22 (P) is shown in fig. 6.

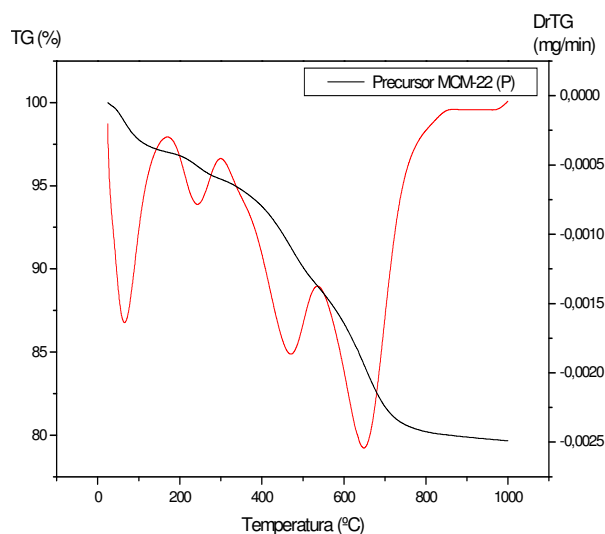


Fig. 6. Curve analysis (TGA) and its derivative to the precursor MCM-22 (P).

For the precursor MCM-22 (P) ranges of mass loss were highlighted:

- 2.95% (up to 167 °C) corresponding to desorption of water, which on the occupation of pores per molecule of director [6].
- 1.66% (174 - 300 °C) and 6.87% (300 - 540 °C) on the loss of organic matter and water coming from condensation of silanol groups.
- 9.95% (540 to 855 °C) associated with the removal of residual organic matter.

### Conclusions

The synthesis of precursors static zeolitic lamellar known as MCM-22 (P) is possible for a period of 10 days at 150 ° C. This precursor was identified by the diffraction of X rays, especially the peaks (001) and (002) representing a lamellar compound. This material when subjected to the calcination process resulted in a crystalline material and pure, zeolite MCM-

22, where the diffraction pattern of X rays showed a better definition of the characteristic peaks.

After the incorporation of metals (Pt, Ni and Pt-Ni) was observed from XRD that there was no change in the characteristic peaks.

By EDX it was possible to confirm that the precursor MCM-22 (P), zeolite Na-MCM-22 and the catalyst Pt/MCM-22, Ni/MCM-22 and Pt-Ni/MCM-22 have high levels of silica compared with other species that are present in the analyzed material.

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