XXV Congresso de Iniciação Científica da Unicamp

October 18 to 20 Campinas | Brazil

Study of preparation and characterization of molecular sieves doped with (Ca)²⁺ and (PO₄)³⁻

Ana Letícia Gondim de Carvalho*, Henrique Brasil, Gustavo Paim Valença.

Abstract

In order to combine the high surface area of MCM-41 to acidic and basic characteristics from the Ca and P in hydroxyapatite, this study aims to study and compare the influence of impregnation of different Ca/P ratios (1,64, 1,67 and 1,70) in the MCM-41's morphology. The molecular sieve was synthesized by LCT method (liquid crystal templating) and impregnated with Ca and P by incipient wetness. The solids were characterized by XRD, N₂ physisorption and NH₃/CO₂ TPD. The impregnation of Ca and P considerably increased the acidic and basic properties of MCM-41 and more strongly influenced the surface acidity, increasing up to 600% the number of acid sites per area.

Key words:

MCM-41, calcium, phosphorous.

Introduction

MCM-41 has favorable characteristics to the catalysis and adsorption study: one-dimensional pore arrangement, large specific surface area and pore volume, weak acidity and good thermal stability¹. On the other hand, hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) has both acidic and basic sites². This work aims to study the influence of the impregnation of different Ca/P ratios on the MCM-41's superficial acidity and basicity.

Results and Discussion

MCM-P presented characteristic reflections, with 3 peaks at 2θ=2.9°, 4.7° and 5.4°, typical of the hexagonal cell of the MCM-41's mesoporous structure (Image 1).

Image 1. X-ray diffractogram of pure MCM-41 (MCM-P).

All the synthesized samples are mesoporous and the MCM-P specific surface area (Chart 1) is compatible with the value found in the literature (700 to 1100 m² g⁻¹)¹.

Chart 1. BET analysis results.

Sample	S _{BET} (m ² g ⁻¹)	D _p (nm)	V _p (cm ³ g ⁻¹)
MCM-P	705	2.54	0.27
MCM-64	141	5.87	0.20
MCM-67	104	5.30	0.13
MCM-70	159	5.90	0.22

The surface area decreased considerably with Ca and P impregnation, which is an indication that Ca/P impregnation has occurred at the surface.

Ca/P impregnation increases the acidity of MCM by more than 600%, possibly due to the Ca²⁺ cations (Lewis

acid)³. Even a small change in Ca/P ratio interferes in the acidic characteristics of the solids (Chart 2).

Chart 2. Acidic sites distribution (%)

Sample	W	M	S	Total (μmol NH ₃ m ⁻²)
MCM-P	47.3	44.7	8.0	0.57
MCM-64	46.4	41.2	12.4	4.10
MCM-67	31.1	22.7	46.2	2.18
MCM-70	50.8	21.0	28.2	3.09

The MCM-41's basicity increases considerably with impregnation. However, the basic sites are not influenced by the different Ca/P ratios (Chart 3). Possibly, the basicity comes from CaO and PO₄³⁻. Once PO₄³⁻ do not have an efficient impregnation on MCM-41 surface⁴, the Ca/P ratio differences became less relevant for basic sites formation.

Chart 3. Basic sites distribution (%).

Sample	W	M	S	Total (μmol CO ₂ m ⁻²)
MCM-P	14.3	1.4	84.3	0.59
MCM-64	31.3	32.8	35.9	1.52
MCM-67	22.2	34.0	43.8	1.56
MCM-70	25.4	24.2	50.4	1.46

Conclusions

The introduction of an acid and basic character allied to a high surface area of MCM-41 produces a material with the potential to be applied in heterogeneous catalysis. The influence of the Ca/P ratio is significant on the MCM-41's surface acidity. The density of the basic sites of the impregnated samples, although superior to the pure compound, showed no relevant differences with the Ca/P ratio, indicating a limited adsorption of the phosphate anion to the MCM-41 surface.

Acknowledgement

To CNPq for providing the scientific initiation grant to the first author.

¹ J. S. Beck et al, *J. Am. Chem. Soc.* **1992**, 114, 10834.

² T. Tsuchida et al. *J. Catal.* **2008**, 259, 183.

³ T. Wang et al. *Micropor. Mesopor. Mat.* **2012**, 148, 184.

⁴ M. Vallet-Regí et al. *Solid State Sci.* **2005**, 7, 233.