

# Catalytic Properties of Lanthanum Ion Bonded to Functionalized MCM-41 in the Hydrolysis of Phosphodiester

Carlos A. A. Vargas (PG), Maria H. Araujo (PQ) and Tiago A. S. Brandão (PQ)\*

Departamento de Química, ICEx, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte/MG

E-mail: caamayav@ufmg.br; tasb@ufmg.br.

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## Abstract

La-MCM-41 was tested as catalyst in the hydrolysis of phosphodiester showing promising results.

## Introduction

In recent decades, the use of ordered mesoporous silica in the catalytic field has received significant attention due to its high surface area, large pore channels and possibility of surface modification.<sup>1</sup> These features have been used for binding metallic ions to the structure of mesoporous silica,<sup>2</sup> and it was chosen by us for La<sup>3+</sup> incorporation. Lanthanide ions are strong Lewis acids, which is useful for catalysis of different types of reactions.<sup>3</sup> The goal of this work is to develop a new heterogeneous catalyst, based on La<sup>3+</sup> and carboxyl-MCM-41, for the hydrolysis of phosphodiester under basic conditions.

## Results and Discussion

The synthesis of the phosphodiester, bis(2,4-dinitrophenyl) phosphate (BDNPP), was made as described by Bunton and Farber.<sup>4</sup> Mesoporous [Si]-MCM-41 molecular sieves was fabricated using the method of Mokhonoana and Coville.<sup>5</sup> The obtained material was then modified according to the procedure described by Luštická et al.<sup>6</sup> (Figure 1).

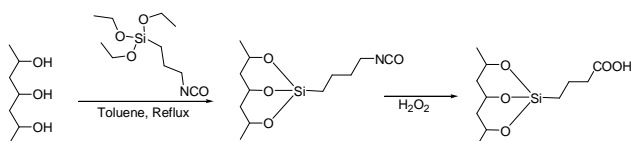


Figure 1. Modification process for the MCM-41.

The modified MCM-41 (100 mg) was combined with 5.0 mL of an ethanolic solution with 100 mmol dm<sup>-3</sup> of LaCl<sub>3</sub>. The solution was refluxed by 24 h to ensure the La<sup>3+</sup> coordination, followed by filtration and extensive washing with EtOH. The resulting La-MCM-41 was dried overnight at 60 °C under vacuum and characterized by thermal analyses.

The La-MCM-41 (50 mg) was used for catalysis of the hydrolysis of BDNPP (20 μmol dm<sup>-3</sup> of a solution 5 mmol dm<sup>-3</sup>) in 20 mL of Hepes buffer solution 0.1 mol dm<sup>-3</sup> at pH 8.0 and 25 °C.

The BDNPP hydrolysis was followed by UV-Vis spectrophotometry (Figure 2) using a flux system and presented a typical consecutive kinetic behavior as shown in Scheme 1.

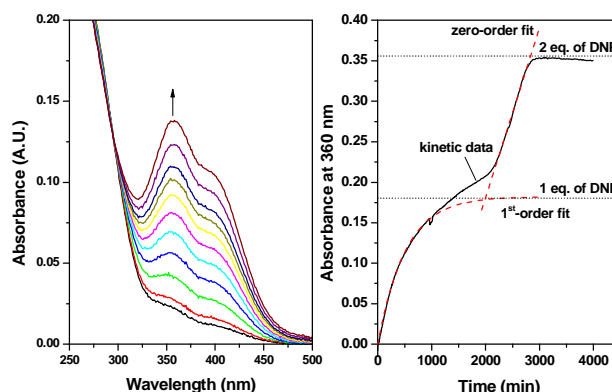
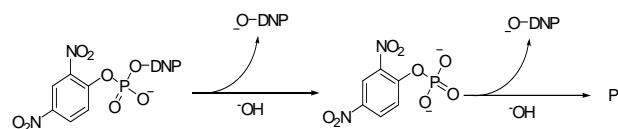


Figure 2. Kinetic data obtained for the hydrolysis of BDNPP using La-MCM-41.



Scheme 1. Reaction pathway for BDNPP hydrolysis.

BDNPP hydrolysis followed a first-order kinetic behavior with a rate constant of  $3.26 \times 10^{-6} \text{ s}^{-1}$  up to the formation of the first DNPO<sup>-</sup> equivalent. This rate constant is about 14-fold higher than reported for the same reaction in absence of catalyst.<sup>4</sup> The subsequent hydrolysis of the phosphomonoester to the second DNPO<sup>-</sup> equivalent and inorganic phosphate exhibited a zero-order kinetic behavior.

These observations indicate that the two hydrolytic reactions occur on the silica surface, and the phosphomonoester formed in the first reaction does not diffuse to the solution before being hydrolyzed. These results are promising and a deeper investigation is underway.

## Conclusions

The modified La-MCM-41 presented good catalytic activity in the hydrolysis of BDNPP.

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