Catalytic activity of the Metal-Organic Framework MIL-101(Cr) for cyanosilylation of aldehydes

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Introduction

The Metal-Organic Framework (MOF) MIL-101(Cr) has been reported as a good catalyst for cyanosilylation reactions.[1] This process constitutes an important step in the preparation of compounds like β-aminoalcohols, α-hydroxyacids, α-hydroxyketons and α-aminoacids, which are very useful in the synthesis of pharmaceuticals and agrochemicals.[2] MIL-101(Cr) is a highly porous solid, with large pores and, therefore, it can be used as heterogeneous catalyst in processes which involve bulky substances, such as molecules of biological interest. Understanding at the molecular level the performance of this MOF as a catalyst in cyanosilylation of aldehydes is extremely important, because it would allow the identification of the characteristics of this material that make the catalysis possible. Thus, the obtained information could help the design of new MOFs that are more efficient or different ways to optimize the catalytic activity of MIL-101(Cr). In this work, the catalytic properties of this material are investigated for the cyanosilylation reaction of aldehydes through DFT calculations.

Methodology

Mechanisms of aldehydes conversion in their respective trimethylsilylated cyanohydrins (cyanosilylation reaction) were performed, through the addition of trimethylsilyl cyanide (Figure 1).

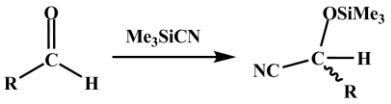

Figure 1. Cyanosilylation of aldehydes.

Five catalyzed mechanisms were studied using models of metallic clusters (Figure 2) to describe the catalytic site of MIL-101(Cr) and three non-catalyzed mechanisms, in order to be compared to the catalyzed processes, were also analyzed.

Figure 2. Metallic clusters to model MIL-101(Cr).

Calculations were performed in Gaussian09 and Turbomole6.5 at PBE/6-311++G(d,p) and PBE/def2-TZVP levels of theory, respectively. The studied mechanisms considered different ways to obtain the desired products through the cyanosilylation of formaldehyde, acetaldehyde and benzaldehyde. Ionic and concerted non-catalyzed and catalyzed mechanisms were studied. Furthermore, the catalytic activity of the MOF MIL-101(Cr) as Lewis acid (Mechanisms 3 and 4) and as Lewis acid and base, it is, as a bifunctional catalyst (Mechanisms 5 and 6), were evaluated.

Results and discussion

The calculated rate constants for all studied mechanisms are presented in Table 1 to formaldehyde, since acetaldehyde and benzaldehyde followed the same trend.

Table 1. Rate constants for mechanisms of cyanosilylation of formaldehyde.

	k / s^{-1}				
	Mech.			Mech.	cat1	cat2
Non-catalyzed	ionic	$>3x10^{-111}$	Catalyzed	ionic	$>3x10^{-111}$	-
	1	$9x10^{-19}$		3	$6x10^{-10}$	$3x10^{-15}$
	2	$6x10^{-26}$		4	Probably it does not occur	
				5	$2x10^{-16}$	-
				6	Probably it does not occur	

The results indicate that both, the catalyzed and the non-catalyzed mechanism, occur through concerted processes, in which there is formation of a transition state with a five-membered cycle (Mechanism 1 and 3) in the limiting step of the reaction. Furthermore, the catalytic performance of MIL-101(Cr) probably occurs due to the presence of Lewis acidic sites, which come from coordinatively unsaturated chromium(III) ions, because Mechanism 3 was observed as the most kinetically favorable process. The catalytic sites might occurs in regions of crystal defects, located in the material structure, or in its surface, since it was observed that the most simple cluster model (Figure 2 (a) – cat1) better explain the catalytic performance of the studied MOF.

Conclusions

The catalytic activity of the MIL-101(Cr) was verified and its catalytic site identified. Furthermore, this study indicate that one way of enhancing the catalytic properties of MIL-101(Cr) would be through their preparation by synthetic routes that lead to defects in this solid structure.

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