Hard acidity and structural constraints in catalysts based on MCM-41

L. D. Cano[1], C. Zicovich-W[2*]., P. Boch-G[3]., V. Gonzalez-V[1]., and J. Aguilar-P[1]
[1] UAM-A, Área de Química Aplicada, D. F., México.[2] Depto. de Física, UAEM, Cuerna. Morelos, México.[3] ICCM, UNAM. México, D.F., [*] claudio@buzon.uaem.mx

Introduction

Acid mesoporous materials behave as effective catalysts in several reactions of industrial interest. Some of these reactions include large-molecule reactants and products, so microporous materials and zeolites do not catalyze reactions in the same manner. Beside their very good diffusive properties, there are evidences that mesoporous materials differ from zeolites in other aspects that involve electronic structure of the active sites [1]. In particular, methylation of naphthalene on H-MCM-41 exhibit a completely different selectivity towards the beta substitution that cannot be attributed to size constraints in the diffusion of reactants or products.[5, 11].

In this work, we explore the possibility that mesoporous materials selectivity could be due to acid hardness of the active sites, in the context of Pearson's theory. We consider several cluster models of the active sites on the surfaces of the MCM-41, and then compute their electronic structures using quantum chemistry methods. We start from the hypothesis that structural disorder in the neighbors of the active site is accompanied by strong distortions in the Si-O lengths, compared to the relaxed situation that occurs in the more flexible zeolite frameworks. It is shown that these distortions give rise to an increase of the active site hardness, here estimated on some theoretical indices such as charges and LUMO energies.

Methods

Used different silicates and MCM-41 for compare the distances between them.

First, we explore interatomic distances of Si-O bridges, using FDR method, for silicates and MCM-41.

Then, we constructed two MCM-41 cluster models, and calculated Si-O distances, HF(Hartree Fock) energy, condensed charges, angles and interatomic distances for each one. We used a 64-processor IBM-RS6000 supercomputer and Gaussian software.

Discussion

From the two cluster models (3-coordinated and 4-coordinated silicates), we found the optimizad molecule in order to know the average Si-O distances (1.54 X and 1.9 X, respectively).

In the figure 1a, we have the tetracoordinated withouth restrictions, mean the bond Si-O has a free movement (1.66X). I the figure 1b, we have the tetracoordinated restinged in one of the bonds, but the other oxygens are free for the movement. In fact, the tetracoordinated is dissociated. When this distance are more and more reduced the site is more hard. We start from the hypothesis that structural disorder in the neighbors of the active site is accompanied by strong distortions in the Si-O lengths, compared to the relaxed situation that occurs in the more flexible zeolite frameworks [2,3,4]. It is shown that these distortions give rise to an increase of the active site hardness [6,7,8,9,10], here estimated on some theoretical indices such as charges and LUMO energies.
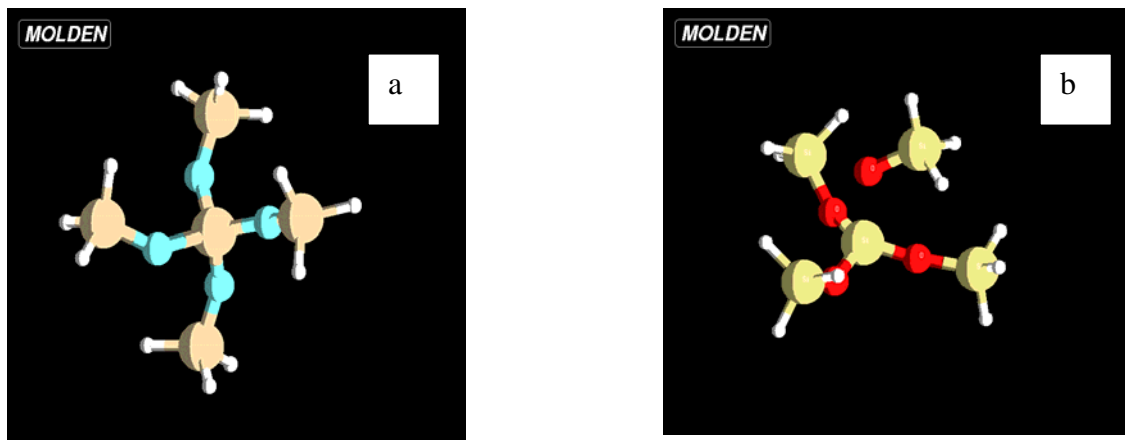
Figure 1. a) the tetracoordinated silicate and b) the dissociated tetracoordinated silicate.

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