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Acidic and basic sites of M_2DEBDC (M = Mg or Mn and E = O or S) acting as catalysts for cyanosilylation of aldehydes

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ABSTRACT

The building blocks of the Metal–Organic Frameworks (MOFs) may have different chemical groups or atoms, thus these solids have quite diversified properties. The understanding at the molecular level of the MOFs in possible applications may allow the design of new optimized materials with specific sites accordingly chosen, by means of the reticular chemistry. The MOFs M_2DEBDC (M = Mg or Mn and E = O or S) are composed by divalent metallic cations connected by 2,5-dihydroxybenzene-1,4-dicarboxylate (DOBDC) or by 2,5-disulfhydrylbenzene-1,4-dicarboxilate (DSBDC). In this work, Density Functional Theory (DFT) calculations were performed to unveiling the strength of the possible acidic and basic sites of M_2DEBDC. The analyses indicated that M_2DSBDC may have more efficient basic sites than M_2DOBDC with the first materials presenting less ionic character. The positive Bader charges over the metallic cations followed the increasing order Mn(II) < Mg(II), suggesting that Mg_2DEBDC contains more efficient acidic Lewis sites than Mn_2DEBDC. The flexibilities of the solid structures occurred in the crescent order: $Mg_2DOBDC < Mg_2DSBDC < Mn_2DOBDC \simeq Mn_2DSBDC$. Considering the experimental evidence that Mn_2DOBDC is a better catalyst than Mg_2DOBDC and the mechanistic results obtained through DFT calculations, the structural flexibility seems to be a more important factor than the electronic factor of the charge to explain the catalytic performance of the materials.

1. Introduction

The porous solids of the Metal–Organic Frameworks (MOFs) class are materials which structure is based on strong bonds between the following building blocks: metallic clusters and divergent organic ligands [1]. The coordination entities of these solids are repeated in the formation of an extending structure [2]. Many different metallic clusters [3] and divergent organic ligands [4] can be combined resulting in more than 70,000 different MOFs already described on Cambridge Structural Database [5]. Besides that, about 137,000 structures were predicted by *in silico* design [6].

The building blocks may have different chemical groups or atoms, then the MOFs present quite diversified properties. This implies the great application potential of these materials in many areas such as gas storage, separation methods, catalysis, sensors, controlled drugs release devices and magnets [7–9]. Metallic clusters and divergent organic ligands can be chosen in order to predetermined structures can be obtained by means of the reticular chemistry [10]. Thus, the understanding at the molecular level of the MOFs for their possible application allow the design of new optimized materials with specific sites accordingly chosen. In this sense, computational simulations to obtain information about the chemical behaviors of the MOFs building blocks are of great relevance.

The topology of MOF-74 [11] (or CPO-27 [12]) is obtained by the combination of divalent metallic cations arranged on six infinity rods connected by divergent organic ligands such as 2,5-dihydroxybenzene-1,4-dicarboxylate (DOBDC). The solids with this topology have one-dimensional channels with diameters around 15 Å. Moreover, in their structures there are a high density of coordinatively unsaturated metallic cations, which could act as acidic Lewis sites [13]. On the other hand, the phenolate or carboxylate groups of the organic ligand could act as basic Lewis sites [14]. These sites are oriented towards the large material channels indicating their high catalytic potential.

These MOFs can be represented by the formula M_2DOBDC, which M is a divalent metallic cation. The DOBDC ligand can also be substituted by 2,5-disulfhydrylbenzene-1,4-dicarboxilate (DSBDC) [15,16], resulting in the substitution of the phenolate by thiophenolate groups in the solid structure. The M_2DOBDC (M = Mn, Mg, Zn, Ni or Co) have been investigated as catalysts for the cyanosilylation of benzaldehyde and it was observed that the best catalysts were M_2DOBDC (M = Mn or Mg) [17]. In this work, to

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unveiling the strength of the possible acidic and basic sites of the M_2DEBDC (M = Mg or Mn and E = O or S), these MOFs were studied performing Density Functional Theory (DFT) calculations. Firstly, the M_2DSBDC (M = Mg or Mn) had their structural and electronic properties deeply understood and compared to the M_2DOBDC (M = Mg or Mn) [18]. Then, the interactions of the four MOFs with water and the reagents of the cyanosilylation of aldehydes were analyzed, as well as the catalytic importance of the materials for this reaction.

2. Methodology

2.1. Models

The investigations of the M_2DEBDC (M = Mg or Mn and E = O or S) were performed with DFT under Periodic Boundary Conditions (PBC). Unless otherwise mentioned, M is Mg or Mn, and E is O or S. The crystalline structures of M_2DSBDC (Fig. 1) were constructed by the substitution of the phenolate by the thiophenolate groups in the Primitive Cell (PC) of M_2DOBDC provided by de Oliveira et al. [18]. The PC is of the P-3 space group and its lattice parameters were converted to R-3 space group (conventional unit cell) to allow comparisons with data available in the literature.

The PCs of M_2DEBDC were used in the study of water adsorption. However, the Supercells (SCs) were used in the investigation of the acidic and basic sites of the materials, by means of the investigation of their importance in the cyanosilylation of aldehydes. The SCs (Fig. 1) were used to avoid interactions between the bulky substrates involved in the reaction of interest in the periodic model. The metallic cations of M_2DEBDC are Coordinately Unsaturated Sites (CUSs) in a square pyramid geometry with potential catalytic activity. The replication of the PC to the constitution of the solid results in a distance between the equivalent CUSs of approximately 7 Å (Fig. S1 in the Supplementary Data (SD)). The SC was proposed to increase this distance, thus avoiding unwanted interactions between the coordinated substrate in a CUS and its replica when the solid is formed from the unit cell. The proposed SCs were constructed by replicating the PCs along their vector *c*, and these crystalline structures came to be considered the unit cells for the representation of the solids. In this way, the equivalent sites become distant by approximately 14 Å (Fig. S1), a value which is more than two times bigger than the largest dimension of the studied substrate benzaldehyde (6 Å). The molecules involved in the studied processes were modeled in a cubic box with 15 Å of edge.

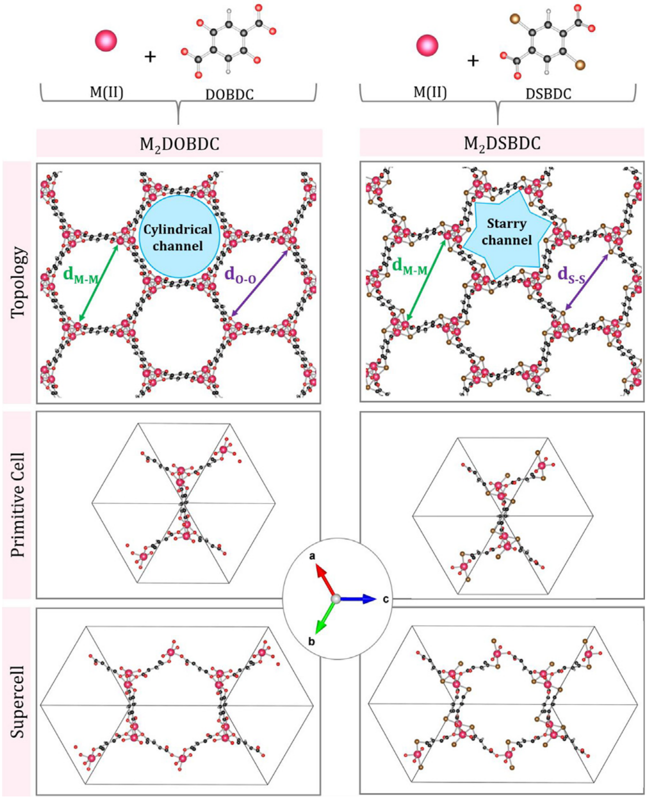

Fig. 1. Topology, primitive cell and supercell of M_2DEBDC (M = Mg or Mg and E = O or S). Legend of atoms: carbon (black), hydrogen (grey), metallic cation (pink), oxygen (red) and sulfur (brown). (Colour online.)

2.2. Computational details

DFT calculations were performed with plane waves methodology under PBC. The exchange–correlation functional PBE [19] with pseudopotential of ultrasoft (US) type were used in the Quantum Espresso package [20]. The PBE pseudopotentials were downloaded from the GBRV [21] library. The D2 method developed by Grimme [22] was included for the dispersion correction. Hubbard parameters were also included for manganese atoms in the simulations of Mn_2DEBDC to better describe the electronic correlation on *d* orbitals, with $U = 5.5$ and $J = 0.0$ eV. The DFT+U calculations were performed with the simplified version of Cococcioni and Girancoli [23]. These values for the Hubbard parameters were observed as the best ones to describe structural and electronic properties of Mn_2DOBDC when the PBE functional and ultrasoft pseudopotentials were used to simulate this material [18], besides affecting in less than 2 kcal mol^{-1} the energies calculated in this work (Section 2 at SD). Therefore, the levels of theory PBE-D2/US and PBE-D2+U5.5+J0/US were used in the calculations of Mg_2DEBDC and Mn_2DEBDC, respectively. The materials constituted by magnesium(II) were simulated as closed shell systems. Those constituted by manganese(II) were simulated considering the metallic cations in the high spin configuration and with antiferromagnetic interactions among the Mn(II) ions along and between the metallic rods. The levels of theory and spin configurations used provided data in agreement with experimental ones, as discussed by de Oliveira et al. [18].

The simulations were carried out using 50 Ry of kinetic energy cutoff for the plane waves and 500 Ry of kinetic energy cutoff for the charge density and potential. The integrations in the first Brillouin-zone were performed at the Gamma point and Marzari–Vanderbilt smearing [24] of 0.02 Ry. Convergences for energies of 1 mRy per atom were guaranteed by these values of the calculation parameters. The convergence criteria to energy and force for the atom positions in the geometry optimizations were 10^{-4} Ry and 10^{-3} Ry $Bohr^{-1}$, respectively. The cell vectors were also optimized. Quantum Theory of Atoms in Molecules (QTAIM) was applied in the analyses of the electronic density topology of the systems, with the calculations performed in the Critic2 program [25].

3. Results and discussion

3.1. Structural and electronic properties of the M_2DSBDC (M = Mg or Mn)

The Mg_2DOBDC and Mn_2DOBDC were firstly prepared by Dietzel et al. [26] and Zhou et al. [27], respectively. The structural and electronic properties of these materials were investigated by de Oliveira et al. [18]. The Mn_2DSBDC was first prepared by Sun et al. [15] and the preparation of Mg_2DSBDC has not been described in literature. In this work, the M_2DSBDC were studied