

Screening of bimetallic M-Cu-BTC MOFs for CO₂ activation and mechanistic study of CO₂ hydrogenation to formic acid: A DFT study



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ABSTRACT

In this work, CO₂ activation and hydrogenation on a series bimetallic M-Cu-BTCs are investigated by density functional (DFT) theory calculations. The hybrid MOFs, namely Mo-Cu-BTC and W-Cu-BTC, with outstanding ability for CO₂ activation are screened out and the mechanisms of CO₂ hydrogenation to formic acid on them are investigated. The calculation results indicate that CO₂ could be activated on W-Cu-BTC and further be hydrogenated through an exceedingly facile pathway when atomic H* is introduced into the system.

1. Introduction

In recent years, the human activities, such as the industrial revolution and the development of transportation, have caused expedited fossil fuels consumption which resulted large amount of CO₂, the primary greenhouse gas, been added into carbon cycle [1,2]. Since that CO₂ can be used as available carbon feedstock for the production of variety of valuable chemicals, the study on the capture and recycling of CO₂ has been focused by scientific researchers [3–8]. Among them, the process of CO₂ hydrogenation into formic acid, as an atom-efficient reaction, has drawn a lot of attentions. Formic acid is an important raw materials and intermediates for many fields, such as the manufacture of leather and the feedstock for fuel cells [9]. In the past few years, formic acid has been taken into account as the hydrogen storage material by combining CO₂ hydrogenation with selective formic acid decomposition [10–12].

In the field of CO₂ capture, the Metal–organic frameworks (MOFs), a class of porous materials with flexible structures and high surface areas, have shown good performance on CO₂ selective capture and separation [13–22]. Furthermore, the MOFs can be used as heterogeneous catalyst owing to its tunable metal center and the organic linker [23]. Hence, the combination of MOFs' the outstanding ability of CO₂ capture and its potential catalytic performance will make MOFs have great potential at CO₂ utilization. Cu-BTC, a copper-based MOFs with favorable structural stability and plentiful unsaturated metal sites, is an efficacious material for CO₂ capture [14]. The Cu-BTC consists of copper carboxylate paddlewheel dimers, [Cu₂(COO)⁴⁻(H₂O)₂], and organic linker, bezene-1,3,5-tricarboxylate (BTC) [24]. Both copper

centers in the paddlewheel dimer are coordinated with a H₂O molecular, which can be removed after heat treatment in order to get unsaturated metal sites acting as active sites for the capture of gas molecules such as NO, CO and CO₂ or the catalysis of chemical reactions [25–28]. In recent years, the synthesis of other porous M-BTC materials, consisting of Fe, Mo, Cr, Ni and Ru, have been reported [29–31], which alter both physical and chemical characteristics of unsaturated metal sites in MOFs. Even so, the strong and unpolarized M–M bond in these structures significantly weakens the activity of unsaturated M cations. In previous simulation studies, it was discovered that bimetallic MOF reveals different electronic property from monometallic MOF, of which the dissymmetry M–M' dimer weakens the M–M bond for the charge polarization between hybrid metal cation [32,33]. Moreover, the experimental studies reported that the M-Cu-BTC (M = Zn or Ru) have been successfully synthesized by replacing Cu with Zn and Ru. Both Zn-Cu-BTCs and Ru-Cu-BTC maintain nearly the same crystal structure with Cu-BTC [34,35]. These researches provide an orientation to exploit new type of M-Cu-BTC which contains activated unsaturated metal sites.

The asymmetrical metallic bond in M-Cu dimer makes the unsaturated metal site distinct from that of the pure M-M-BTC. By using the density functional theory calculations, the exploration of the CO₂ adsorption ability of multiple M-Cu-BTC MOFs can be carried out systematically and rapidly. And the bimetallic MOFs which pare capable of efficiently adsorbing and chemically activating of CO₂ can be screened out. In present work, we first conduct a DFT study on the adsorption of CO₂ on series transition metal substituted M-Cu-BTC (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au) and

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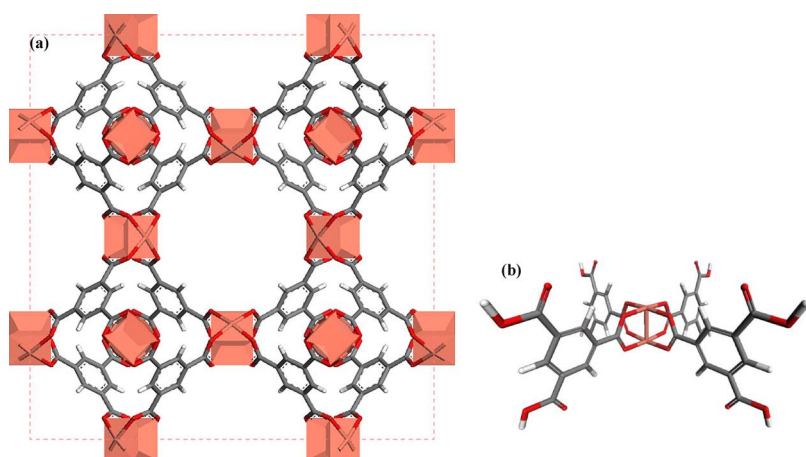


Fig. 1. Structure of periodic model (a) and cluster model (b) of Cu-BTC. Color code: Orange, Copper; Red, Oxygen; Gray, Carbon; White, Hydrogen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

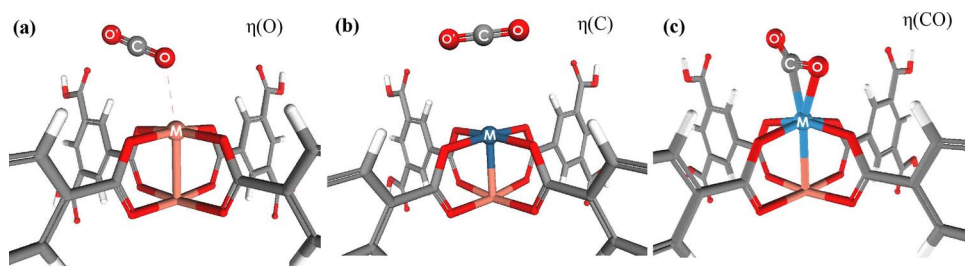


Fig. 2. Three adsorption configurations of CO₂ on M-Cu-BTC. (a) represent CO₂ linear type adsorption via η(O); (b) represent the adsorption via η(C); (c) represent activated adsorption via η(CO).

pick out the M-Cu-BTC MOFs which are capable of activating CO₂. Then we map out the mechanism of formic acid synthesis from CO₂ hydrogenation on the selected potential M-Cu-BTCs.

2. Computational details

There are 624 atoms in the unit cell of Cu-BTC (see Fig. 1a), which include 48 coppers, 192 oxygens, 288 carbons and 96 hydrogens. A cluster model (see Fig. 1b) containing a “paddlewheel” structure with the formula of Cu₂O₈C₂₈H₂₀ is chosen to reduce computational resource needed in this study [32,36,37]. Furthermore, such model has been successfully employed by Liu and co-workers in the study of CO adsorption on Cu-BTC [38], which received almost identical results with it on periodic model [39].

All density functional theory (DFT) calculations in this work were accomplished by Dmol3 package in Materials Studio [40,41] with DNP basis set. As for the exchange-correlation functional, the GGA-PW91 method was chosen, which has been confirmed appropriate for our system in previous works [32,36,42]. The space cut-off radius was set as 4.5 Å and OBS method was adopted for DFT-D correction. The geometry optimization was performed until the energy, force and displacement on each atom was converged to less than 2.0×10^{-5} Ha, 4.0×10^{-3} Ha/Å, 5.0×10^{-3} Å, respectively. The molecule adsorption energy (E_{ads}) was defined according to the following equation:

$$E_{\text{ads}} = E_{\text{MOF/X}} - E_{\text{MOF}} - E_{\text{X}}$$

where $E_{\text{MOF/X}}$ represents the total energy when “X” molecules adsorbed on MOFs, E_{MOF} means the energy of MOFs with no “X” molecules adsorption, while E_{X} is the energy of dissociative “X” molecules.

The activation barrier E_{a} is defined as:

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{Coads}}$$

where, E_{Coads} and E_{TS} refer to the total energies of co-adsorption and transition states, respectively. Each transition state (TS) in this work has been verified to have only one imaginary vibration.

3. Results and discussion

3.1. Screening of bimetallic MOFs

The transition metals of I, II, VI, VII, VIII subgroups from Row 4 to Row 6 in Periodic Table of Elements except for Hg have been taken into account to create the M-Cu-BTC model through the replacement of a Cu atom in Cu-BTC. Several adsorption modalities are investigated to get the most stable adsorption configuration for each M-Cu-BTC (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au). The bimetallic MOFs which are able to activate CO₂ will be screened out, and their H₂ adsorption performance and electronic properties are further investigated.

3.1.1. Adsorption of CO₂ on different M-Cu-BTCs

We have considered three adsorption configurations (η(O), η(C), η(CO)) of CO₂ (see Fig. 2) on M-Cu-BTCs and the most stable structures are elected, and the results (structure parameters and adsorption energies) are summarized in Table 1. Among most of the 20 M-Cu-BTC candidates, CO₂ binds the adsorbents via the long pair of O atom to M metal sites, in which CO₂ molecule still maintains its linear type (see η(O) in Fig. 2). For instance, CO₂ molecule attaches to Cu-BTC with a distance between O and Cu atoms of 2.490 Å. The angle of Cu...O–C is 121.44° and the angle of O₂–C–O is 179.19°. In addition, the C–O bond is mildly stretched from 1.164 Å to 1.179 Å. There are fourteen M-Cu-BTCs adsorbing CO₂ as η(O) configuration. Among them, the adsorption of CO₂ on Ru-Cu-BTC has the highest binding energy of –0.59 eV, and the adsorption on Au-Cu-BTC is the weakest with a binding energy of –0.20 eV which is still slightly higher than that of Cu-BTC (–0.19 eV). In the η(C) model, the distance of CO₂ molecule and M site is larger than that of the other two configurations leading to the weaker interaction between C atom and M site. For example, when adsorbs on the Pd site of Pd-Cu-BTC, CO₂ remains its original linear structure with a distance between C and M atoms of 3.135 Å, and the adsorption energy is just –0.13 eV. CO₂ adsorbs on M site via the M–C and M–O bonds as a bidentate configuration (η(CO) model) in W-Cu-BTC, Mo-Cu-BTC, Re-Cu-BTC and Os-Cu-BTC. For example, when CO₂

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