Metal paddlewheels as sensors for detection of SO₂ gas: a DFT study

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Abstract
The sensing properties of the paddlewheel-type metal dimer (M-BTC: M = Fe, Ni, Cu, Zn, and Pd) toward SO₂ gas were theoretically investigated using density functional theory (DFT) at the M06-L level of theory. Single-point calculations were carried at the M06 functional to correct the energetic properties and HOMO–LUMO energy gap. The O-bound adsorption complex of SO₂ on the metal center of paddlewheels is found to be thermodynamically favorable than the S-bound ones. The trend of adsorption energy of SO₂ on the metal center is in the order Pd-BTC < Cu-BTC < Ni-BTC < Zn-BTC < Fe-BTC. Among these five paddlewheels, the Ni-BTC and Zn-BTC paddlewheels are highly sensitive toward SO₂ gas as compared to the other systems. The density of states reveals that the adsorption process significantly reduces the LUMO of the system to lower energies, enhancing the conductivity of the system. From DFT results, the energy gap of Ni-BTC and Zn-BTC is significantly reduced by 18.0 and 41.0% after the adsorption of SO₂ on the metal center. These results suggest the great potential of Ni-, and Zn-BTC paddlewheels as SO₂ sensors.

Introduction
After the industrial revolution, the air pollutants which are mainly released from various processes from petrochemical industries, coking plants, waste treatment units, etc., turn into a global concern. Harmful gases such as sulfur-containing gases, nitrous oxide (N₂O), and carbon dioxide (CO₂) are principal contributors to effect on the environment, such as acid rain, global warming, and climate change. Various approaches have been proposed to reduce the unprecedented levels of these harmful gases (Peter 2018; Zhang et al. 2020). Sulfur dioxide (SO₂), which is an irritant colorless gas, is regarded as one of the most harmful gases. The burning of fossil fuels containing sulfur such as coal, oil, and diesel from vehicles, power plants, and industrial factories is the primary source of SO₂ emission. To control the emission of SO₂ effectively, SO₂ sensors are necessary to monitor and track the presence of SO₂ in the environment. Therefore, great efforts have been devoted to finding out gas-sensing materials for SO₂ detection.

Various materials such as metal oxides (Ji et al. 2019; Zhou et al. 2019), metal sulfides (Tang et al. 2020; Zhang...
and carbon-based nanomaterials (Kumar et al. 2017; Shen et al. 2013) have been employed as sensor materials for SO₂ gas. Among materials for sensing applications, metal–organic frameworks (MOFs) have attracted great interest in applications not only gas adsorption/sepation, catalysis but also sensing applications (Bien et al. 2019; Chernikova et al. 2018; Furukawa et al. 2013; Kokcam-Demir et al. 2020). Pohle et al. (2011) investigated the utilization of Cu-BTC as a gas sensor based on work function changes. The experimental results revealed that Cu-BTC on the Au back electrode was sensitive toward NH₃, H₂S, ethanol, acetone gases at the temperature of 80 °C. Several MOF materials were tested as gas sensors for detecting gases (Achmann et al. 2009). Among studied MOFs (Al-BDC, Fe-BTC, Cu-BTC materials), Fe-BTC is identified to be an appropriate sensor for hydrophilic gases such as water, methanol, and ethanol. However, Fe-BTC did not respond to O₂, CO₂, C₃H₈, NO, and H₂ gases. Recently, a composite of Ni-BTC and OH-functionalized single-walled carbon nanotubes (OH-SWNTs) was synthesized to test the sensing performance for sulfur dioxide (SO₂) detection (Ingle et al. 2020). The composite sensor exhibits selectivity to SO₂ gas as compared to other tested analytes as CH₄, CO, and C₂H₂ gases. From the experimental study, it was found that the composite has a detection limit of 4 ppm with a response time and a recovery time of 5 and 10 s, respectively. Here, inspired by the Ni-BTC-based sensor, the gas sensitivity of the paddlewheel-type di-metal center unit can be modified by adjusting the type of metal as similar as done for the improvement of MOFs in catalysis. The sensing performance of metal-paddlewheel clusters has not yet been demonstrated from the theoretical viewpoint. Based on DFT calculations, these results could provide deeper insight into the interaction between gases on the metal center of paddlewheel units and reveal some clues for metal-paddlewheel-based gas sensor design.

In this study, a theoretical investigation was employed to get insights into the potential ability of metal-paddlewheel units as SO₂ gas sensors. Five metal-paddlewheel units, namely, Fe-BTC, Ni-BTC, Cu-BTC, Zn-BTC, and Pd-BTC were selected to study the effect of metal properties on SO₂ adsorption. The adsorption energies, charge transfer, and electronic properties were calculated to investigate the sensitivity of these paddlewheels to detecting SO₂ gas. The results of this study could be beneficial for developing metal-paddlewheel-based sensors for detecting this harmful gas.

### Methodology

The adsorption of SO₂ gas on the metal center of paddlewheel units was theoretically investigated using M06-L functional (Zhao and Truhlar 2006, 2007, 2011). The M₂(BTC)₄ cluster, which was obtained from the experimental single-crystal diffraction (XRD) data (Chui et al. 1999), was adopted as the active center of the paddlewheel-based MOFs. The dangling bonds at the terminal -COO groups were saturated with hydrogen atoms as done in previous studies (Kettrat et al. 2017; Maimom et al. 2019; Sirijaraensre 2019, 2021; Verma et al. 2013). Five clusters of paddlewheel units namely Fe-, Ni-, Cu-, Zn-, and Pd-BTC units were selected to investigate the adsorption property and sensing performance for SO₂ gas. For computations, the M06-L functional, which has been widely applied to study the interaction of molecules on the metal center of metal–organic frameworks (MOFs) (Grissom et al. 2019; Injongkol et al. 2017; Li et al. 2019; Paluka et al. 2020; Sirijaraensre 2019, 2021; Verma et al. 2013; Yadnum et al. 2013), was used with the combination of 6-31G(d,p) for non-metal atoms and the Stuttgart-Dresden ECP (SDD) for transition metal atoms, respectively. The electronic ground states of M-BTC (M = Fe, Ni, Cu, Zn, and Pd) are nonet, triplet, triplet, singlet, and singlet spin states, respectively. For geometry optimization, convergence criteria, which are gradients of maximum force, RMS force, maximum displacement, and RMS displacement, are 0.000450, 0.000300, 0.001800, and 0.001200, respectively. For energy calculations, the SCF convergence criterion of 10⁻⁸ a.u. along with ultrafine integration grid for the integrals was used for all calculations. During optimization, adsorbing molecules and M₂(BTC)₄ cluster were allowed to relax which terminating hydrogen atoms were kept fixed. To obtain a more reliable width of the energy gap, single-point calculations were performed using the M06/6-311G(d,p)+SDD level. Reported adsorption energies at the M06 level were corrected by the counterpoise method to correct the adsorption energy for the basis set superposition error (BSSE) (Boys and Bernardi 2006; Simen et al. 1996). The adsorption energy (E_ads) is calculated from the following equation:

$$E_{\text{ads}} = E(\text{complex}) - E(M - BTC) - E(SO_2) + E(\text{BSSE})$$ (1)

Atomic charges were analyzed by natural bond orbital (NBO) population analysis (Weinhold 2012). All calculations were done by using the Gaussian 09 program (Frisch et al. 2009). The plots of the density of states (DOS) were obtained using the GaussSum program to reveal the change of electronic structures of adsorption complexes (O’Boyle et al. 2008).

### Results and discussion

From the experiment, the energy gap (E_g) of Cu-BTC MOF was experimentally reported to be 3.6 eV (Gu et al. 2015). Based on the optimized structure of the Cu-BTC cluster,
the energy gap based on the M06-L calculation is predicted to be 1.21 eV which is significantly lower than the experimental value. To obtain a more accurate prediction of the energy gap, single-point calculations were performed on M06-L-optimized structures by using hybrid M06 functional at the combination of 6-311G(d,p) + SDD ECP basis sets. The M06-calculated energy gap of the Cu-BTC cluster was predicted to be 3.55 eV which is consistent with the experimental observation (Gu et al. 2015). Therefore, all reported values in this work were obtained by using the M06//M06-L level of theory. The M06 functional predicts the energy gap of M06-L-optimized Fe-BTC, Ni-BTC, Zn-BTC, and Pd-BTC clusters to be 2.33 eV, 3.73 eV, 5.63 eV, and 3.21 eV, respectively.

Optimized structures of adsorption complexes are shown in Figs. 1 and 2. The adsorption of SO₂ molecules on the metal site of five metal-paddlewheel units was investigated by the M06//M06-L level of theory. For SO₂ adsorption, there are two possible configurations of the adsorbed sulfur dioxide (SO₂) for interacting with the metal center of metal-paddlewheel units. One is the interaction between the SO₂ molecule on the metal center of paddlewheel units via a terminal oxygen atom (O-bound complex). The other is the interaction via the central sulfur atom of the SO₂ molecule (S-bound complex). For the former configuration, the distance between the SO₂ oxygen atom and the metal center of paddlewheel units increases from 1.947 Å (Fe-BTC) to 2.648 Å (Pd-BTC). After the adsorption, two S–O bonds become inequivalent in which an S–O bond of SO₂ molecule elongates from 1.463 Å to 1.495 Å for the adsorption on Fe-BTC, Ni-BTC, Cu-BTC, Zn-BTC, and Pd-BTC paddlewheels, respectively. The adsorption energy for SO₂ on the metal center in the O-bound complex increases as follows: Pd-BTC (–2.90 kcal mol⁻¹) < Cu-BTC (–6.66 kcal mol⁻¹) < Ni-BTC (–12.01 kcal mol⁻¹) < Zn-BTC (–13.60 kcal mol⁻¹) < Fe-BTC (–19.60 kcal mol⁻¹).
For the S-bound configuration, the SO$_2$ molecule was attached to the metal center of paddlewheels via the lone pair centered on the sulfur atom. This mode of adsorption was not found for the adsorption of the Cu-BTC paddlewheel. Starting from the adsorption on the Cu of Cu-BTC via its sulfur atom, the molecule was optimized to bind with BTC ligands via hydrogen bonds, as shown in Fig. 2. The adsorption energy is predicted to be $-4.16$ kcal/mol, which is smaller than the adsorption of SO$_2$ via its oxygen atom. For the other cases, the S–O bonds of adsorbed SO$_2$ are insignificantly distorted from the isolated values for the adsorption on the metal center of paddlewheel units. Much weaker adsorption energies ranging from $-0.68$ to $-4.42$ kcal/mol were found for the adsorption of SO$_2$ molecules on the Fe-, Ni-, Zn-, and Pd-BTC paddlewheels. Among five metal paddlewheels, Pd-BTC weakly interacts with the SO$_2$ molecule both in O-bound or S-bound configurations. These findings agree with the previous studies of the adsorption of SO$_2$ on the coordinatively unsaturated metal center of MOFs ($-21.77$ for Mg-MOF-74 (Tan et al. 2017), $-17.22$ kcal mol$^{-1}$ for Zn-MOF-74 (Tan et al. 2017), and $-15.79$ kcal mol$^{-1}$ for Zn(BDC)(ted)$_0.5$ (Tan et al. 2013)), in which the SO$_2$ molecule adsorbs on the metal center via its oxygen atom. From calculated results, Fe-BTC paddlewheel has relatively high adsorption energy for SO$_2$ molecules both in O-bound and in S-bound configurations, indicating that SO$_2$ molecule is captured facilely by Fe-BTC paddlewheel.

Electronic properties of SO$_2$ adsorption complexes

Attempts have been made to investigate the change of electronic properties of metal paddlewheels after the adsorption of SO$_2$ molecule. Based on the adsorption energies between the O-bound and S-bound complexes, the O-bound complex is energetically preferred for the adsorption on the metal-paddlewheel clusters. From NBO analysis, the NBO charge of the metal center is predicted to be $+1.122e$, $+1.037e$, $+0.996e$, $+1.277e$, and $+0.711e$ for Fe(II), Ni(II), Cu(II), Zn(II), and Pd(II) cations in the paddlewheel clusters, respectively. NBO analysis reveals the amount of electron transfer and the orbital interaction between the adsorbing molecule and the metal center of metal-paddlewheel units. The results from the NBO analysis are tabulated in Table 1. Excepting the adsorption on the Fe-BTC, the charge of the adsorbed SO$_2$ molecule changes from zero to $+0.024e$, $+0.080e$, $+0.127e$, and $+0.096e$ for the adsorption on Pd-BTC, Cu-BTC, Ni-BTC, and Zn-BTC, respectively. The NBO results indicate that the SO$_2$ gas molecule acts as an electron donor molecule for the adsorption on the Pd-, Cu, Ni-, and Zn-BTC paddlewheels. For Fe-BTC, the HOMO and LUMO orbitals of Fe-BTC are localized on the metal centers of Fe-BTC. Fe centers of Fe-BTC can either provide electrons from the metal center or accept electrons. The direction of electron transfer between the Fe-BTC to the adsorbed SO$_2$ molecule is attributed to the Lewis character of Fe in the paddlewheel. From the FMO diagram, the ILUMO$_{Fe-BTC}$ – HOMO$_{SO_2}$ gap and the ILUMO$_{SO_2}$ – HOMO$_{Fe-BTC}$ is predicted to be 5.73 eV and 2.47 eV, respectively. It was found that the gap of ILUMO$_{Fe-BTC}$ – HOMO$_{SO_2}$ is larger than the ILUMO$_{SO_2}$ – HOMO$_{Fe-BTC}$ gap. Therefore, it might be expected that the electron transfer from the Fe center to the SO$_2$ molecule is the preferable route. NBO analysis showed that 0.247e was transferred from Fe-BTC to the adsorbed SO$_2$ molecule, suggesting that SO$_2$ acts as an electron acceptor molecule. Furthermore, the spin density localized on atoms of adsorbed SO$_2$ is increased as compared with the isolated SO$_2$ molecule. For S-bound configuration, the charge of adsorbed SO$_2$ molecule becomes positive after the adsorption on the Fe-, Ni-, Zn- and Pd-BTC paddlewheels, indicating the SO$_2$ molecule behaves as a nucleophile.

Table 1 The adsorption parameters of SO$_2$ adsorbed on five metal paddlewheels

| System | Configuration | $E_{ads}$ (kcal/mol) | Wiberg bond order of S–O bonds | $Q_T^a$ (e) | $\Delta q(M)^b$ (e) |
|--------|---------------|----------------------|--------------------------------|--------------|-------------------|
| Fe-BTC | O-bound       | $-19.60$             | 1.10, 1.42                     | $-0.247$     | $0.039$           |
|        | S-bound       | $-4.42$              | 1.43, 1.43                     | $0.118$      | $-0.358$          |
| Ni-BTC | O-bound       | $-12.01$             | 1.38, 1.61                     | $0.127$      | $-0.122$          |
|        | S-bound       | $-2.82$              | 1.53, 1.53                     | $0.289$      | $-0.476$          |
| Cu-BTC | O-bound       | $-6.66$              | 1.41, 1.58                     | $0.080$      | $-0.088$          |
|        | S-bound       | $-4.16$              | 1.52, 1.53                     | $0.016$      | $-0.010$          |
| Zn-BTC | O-bound       | $-13.60$             | 1.32, 1.60                     | $0.096$      | $-0.105$          |
|        | S-bound       | $-0.68$              | 1.53, 1.53                     | $0.153$      | $-0.186$          |
| Pd-BTC | O-bound       | $-2.90$              | 1.47, 1.53                     | $0.024$      | $-0.052$          |
|        | S-bound       | $-2.18$              | 1.45, 1.45                     | $0.036$      | $-0.235$          |

$^aQ_T$ refers to the amount of electron transfer between the SO$_2$ to the metal paddlewheel. Positive and negative values indicate SO$_2$ molecule acts as electron donor and acceptor, respectively.

$^b\Delta q(M)$ is the difference NBO charge of the metal center before and after the adsorption of SO$_2$. Positive and negative values indicate the metal center acts as electron donor and electron acceptor, respectively.
donating an electron to the LUMO orbital of the paddlewheel. As a result, the net charge of SO\(_2\) is +0.118e, +0.289e, +0.153e, and +0.036e for the adsorption on Fe-, Ni-, Zn-, and Pd-BTC paddlewheels, respectively. The atomic charge of metal is changed in accordance with the direction of electron transfer between SO\(_2\) molecule and metal paddlewheels as shown in Table 1. Excepting the O-bound complex on the Fe-BTC paddlewheel, the adsorption of SO\(_2\) on the paddlewheels results in a decrease of positive charge of the metal center. From NBO population analysis, it was found that there is no correlation between the adsorption energy of SO\(_2\) and the amount of electron transfer between the SO\(_2\) molecule and the substrate.

From the frontier molecular orbitals (FMO) viewpoint (cf. Fig. 3), the highest occupied molecular orbital (HOMO) of SO\(_2\) shows the participation of all three atoms of the SO\(_2\) molecule. Either O atom or S atom of SO\(_2\) molecule can act as an electron donor center to the available unoccupied orbital of the metal center. The adsorption energy of the S-bound configuration on M-BTC paddlewheels (M = Fe, Ni, Cu, and Zn) is much smaller than the adsorption energy of the O-bound configuration in the corresponding systems. NBO population analysis reveals that the NBO charge of oxygen atoms and the sulfur atom of SO\(_2\) molecule is −0.758e and +1.517e, respectively. From the electrostatic viewpoint, the metal center having a higher charge density tends to have a stronger interaction with a negative charge of the SO\(_2\) oxygen atom. Therefore, the adsorption energy of SO\(_2\) adsorbed on Ni-BTC, Zn-BTC, and Fe-BTC is significantly greater than that on Cu-BTC and Pd-BTC. On the other hand, the more positive charge the metal center, the weaker the SO\(_2\) via its sulfur atom is adsorbed on the metal center. The weak interaction between the metal center and the SO\(_2\) molecule in the S-bound configuration is due mainly to the electrostatic repulsion between the positive charge of metal and the positive charge of the SO\(_2\) sulfur atom. It could be summarized that the interaction between the SO\(_2\) molecule and the metal cluster is mainly governed by the electrostatic interactions, corresponding with the adsorption of styrene oxide on metal-paddlewheel clusters as reported previously (Sirijaraensre 2019, 2021).

SO\(_2\) sensing properties of M-BTC paddlewheels (M = Fe, Ni, Cu, Zn, and Pd)

The DOS analysis was used to provide more detailed data of electronic structure and the contribution of atomic orbitals to the chemical bonds. The DOS plots for the non-interacting system of five metal paddlewheels and SO\(_2\)-adsorption complex in the O-bound configuration on five metal paddlewheels are illustrated in Figs. 4, 5, 6, 7, and 8. After the adsorption of SO\(_2\) on the metal center of paddlewheels, the huge change in PDOS of adsorbed SO\(_2\) happens for the adsorption on the Fe-, Ni, Cu, and Zn-BTC paddlewheels. For the adsorption on Fe-BTC, the peak at the energy of −6.16 eV, which is the HOMO state of the adsorption complex, shows the strong hybridization between the Fe d-orbitals and the orbitals of the SO\(_2\) molecule. As a result, the peak of the energy at −3.60 eV in spin β, which is a π* antibonding orbital of SO\(_2\) molecule, is reduced by half.
Fig. 5 Plots of the density of states projected on $spd$-orbitals of $SO_2$ molecule and $p$, $d$-orbitals of Ni atom in the non-interacting system and the O-bound adsorption complex. The asterisk indicates the position of the displayed MO orbital in the DOS plot.

Fig. 6 Plots of the density of states projected on $spd$-orbitals of $SO_2$ molecule and $p$, $d$-orbitals of Cu atom in the non-interacting system and the O-bound adsorption complex. The asterisk indicates the position of the displayed MO orbital in the DOS plot.

Fig. 7 Plots of the density of states projected on $spd$-orbitals of $SO_2$ molecule and $p$, $d$-orbitals of Zn atom in the non-interacting system and the O-bound adsorption complex. The asterisk indicates the position of the displayed MO orbital in the DOS plot.

Fig. 8 Plots of the density of states projected on $spd$-orbitals of $SO_2$ molecule and $p$, $d$-orbitals of Pd atom in the non-interacting system and the O-bound adsorption complex.
as compared to that of the non-interacting system, indicating
that the electrons of the Fe-BTC paddlewheel partially fill in
the LUMO orbital of SO₂ molecule (cf. Fig. 4). This leads
to the elongation of the S–O bonds. The Wiberg bond order
of S–O bonds is changed from 1.55 in the isolated molecule
to 1.10 and 1.42, respectively. The result shows that a S–O
bond of adsorbed SO₂ has a single bond character. Excepting
the Fe-BTC system, the SO₂ adsorption introduces an impu-
ritly state, which becomes the LUMO state of the adsorption
complex. Besides the electrostatic interaction between the Ni
center of Ni-BTC and the oxygen atom of SO₂, it was found
that there is a σ-donation interaction from the SO₂ HOMO
orbital to the empty Ni-3d orbital as shown in Fig. 5. The
hybridization between two orbitals appears in the DOS pot at
the energy of −12.44 eV. As a result, the Wiberg bond order
of S–O bonds is reduced to be 1.38 and 1.61, respectively.

Unlike the SO₂-adsorption on Fe-BTC and Ni-BTC, the
overlap of SO₂ orbitals and d-orbitals of Zn and Cu cat-
ions creates a small hybridization at the energy of −16.2 eV
and −12.3 eV, suggesting the small electron transfer exists
between HOMO orbital of SO₂ molecule and unoccupied
d-orbital of these paddlewheels (cf. Figs. 6, 7). The PDOS
analysis is consistent with the quality of electron transfer
between two fragments as shown in Fig. 9. Most of the elec-
tron density difference is observed at the adsorbed SO₂ frag-
ment greater than the bond between the SO₂ oxygen atom
and the metal center of paddlewheels. In the case of Zn-BTC
system, the more polarization of adsorbed SO₂ molecule is
mainly induced by the Zn(II) cation in the paddlewheel unit.
These results suggest that the interaction between SO₂ and
Zn-BTC in the O-bound configuration is more ionic than
that found in the Fe-BTC system. The attachment of SO₂ to
the Zn center of the Zn-BTC paddlewheel not only results in
the distortion of the SO₂ molecule but also leads to modi-
fication of the TDOS of the system as compared to that of
the non-interacting system. For the adsorption of SO₂ on the
Pd-BTC (cf. Fig. 8), the PDOS plots for the s-, p-, d- orbit-
als of the metal atom of the non-interacting system and the
SO₂ adsorption complex are almost identical, indicating that
there is no strong orbital interaction between the adsorbed
molecule and the metal center.

The change in the energy difference between the HOMO
energy and the LUMO energy (Eg), affected by the adsorp-
tion of the targeted molecule is used to be a proper indi-
cator to predict the gas-sensing performance of materials
as described in the following equation (Behmagham et al.
2016; He et al. 2020; Peyghan et al. 2013):

\[ \sigma \Delta G \exp \left( -\frac{E_g}{k_B T} \right) \]

From the equation, a slight change in energy gap (Eg)
results in a significant change in electronic conductiv-
ity (σ) of a system. Based on the calculated adsorption
energies, the trend of energies for the SO₂ adsorption
on the metal center via O-bound configuration is Pd-
BTC < Cu-BTC < Ni-BTC < Zn-BTC < Fe-BTC, respec-
tively. Even though, Fe-BTC has the strongest interaction
with the SO₂ molecule, the Eg of the Fe-BTC paddlewheel
adsorbed by the SO₂ molecule is insignificantly changed
by −0.02 eV (−0.8\%) as compared to the Eg of isolated
Fe-BTC paddlewheel (cf. Fig. 4). Similarly, the Eg of Cu-
BTC after the adsorption of the SO₂ molecule on the Cu
center is also identical to that of the isolated Cu-BTC pad-
dlewheel (cf. Fig. 6). The calculated results indicate that
Cu-BTC and Fe-BTC paddlewheels are not appropriate
metal-paddlewheel-based centers for SO₂ sensors. Because
of the strong interaction with the SO₂ molecule, it sug-
gests that Fe-BTC is one of the candidate metal paddle-
wheel as an SO₂ adsorbent. From the population analysis,
the Eg of Ni-BTC and Zn-BTC paddlewheels is changed
after adsorbing SO₂ gas. The Eg is decreased by −0.17 eV
(−5.3\%), −0.67 eV (−18.0\%), and −2.31 eV (−41.0\%) for
the adsorption of SO₂ on Pd-BTC, Ni-BTC, and Zn-BTC
paddlewheels, respectively.
of SO₂ on Pd-BTC is very weak as compared to that on Ni-BTC and Zn-BTC systems. Therefore, this effect has a small influence on the conductivity of the system. These calculated results showed that Ni-BTC and Zn-BTC paddlewheels display sensitivity to SO₂ gas as sensors.

Conclusion

Five metal paddlewheels namely, Fe-BTC, Ni-BTC, Cu-BTC, Zn-BTC, and Pd-BTC were selected to investigate the adsorption of SO₂ gas and the sensing performance by using the M06//M06-L level of theory. Interactions between the SO₂ molecule and the metal center of paddlewheels were determined through adsorption energies, structural parameters, and electronic structures. Excepting the adsorption on the Pd-BTC, the adsorption of SO₂ in the O-bound configuration is preferable rather than the S-bound configuration. The trend of adsorption energies of O-bound configuration is Fe-BTC > Zn-BTC > Ni-BTC > Cu-BTC > Pd-BTC. Even though, Fe-BTC is found to be an effective center for SO₂ capture, the electronic properties of Fe-BTC are slightly sensitive to this gas. Therefore, the Fe-BTC paddlewheel is not a candidate for the SO₂-sensor devices. Among selected paddlewheels, Ni-BTC and Zn-BTC exhibit excellent sensitivity to detect sulfur dioxide (SO₂). The chemisorption of SO₂ gas on the metal center of Ni-BTC and Zn-BTC influences the electronic structure of paddlewheels. As a result, the E_g significantly reduces about 18.0 and 41.0% upon the SO₂ adsorption process on the Ni-BTC and Zn-BTC paddlewheels, respectively. The calculated results will open the way for improving the SO₂ sensor based on metal paddlewheels.

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Author contributions
JS Conceptualization, Methodology, Investigation, Visualization, Writing.

Declarations

Conflicts of interest
The author declares that there is no conflict of interest.

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