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Digest paper

Hybrid computational approaches for deriving quantum mechanical insights into metal–organic frameworks

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ABSTRACT

Experimental studies have increasingly shown that metal–organic frameworks (MOFs) serve as excellent catalytic platforms for various organic reactions. Although the theoretical description of large MOF systems presents a major technical challenge, the hybrid QM/MM computational approach, which has proven highly useful in studying large systems such as enzymes, should have great potential for elucidating fundamental details of MOFs. It is also possible to combine two different levels of QM methods (QM/QM′). This digest paper reviews the applications of these hybrid approaches, which have been made to study catalysis and gas adsorption of MOF systems.

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Introduction

Hybrid quantum mechanics and molecular mechanics (QM/MM) calculations have proven to be highly useful in investigating atomistic details of molecular systems that are too large to be treated fully quantum mechanically. Many research groups have thus far applied QM/MM methods to biological molecules, homogeneous and heterogeneous inorganic systems, and many other systems to uncover their intricate molecular mechanisms.[1] In particular, one of the most intriguing but elusive aspects of these systems is how chemical reactions take place within their complex molecular architectures. The quantum mechanical treatment of a high-prioritized subsystem in QM/MM approaches permits investigation of chemical reactions. Because of this feature, QM/MM methods should essentially be applicable to chemical reactions within metal–organic frameworks (MOFs),[2] which contain an

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overwhelming number of atoms but constitute an interesting class of nanoporous materials.[3] Two different levels of QM methods may also be combined (QM/QM′) to deal with MOFs. Despite the potential of QM/MM and QM/QM′ for deriving microscopic insights into MOF-catalyzed reactions and other processes such as gas adsorption/separation/storage, only a handful of studies along these lines have been undertaken. In this digest paper, we briefly review the applications of QM/MM and QM/QM′ methods to problems pertaining to catalysis and gas adsorption of MOF systems.

QM/MM studies of chemical reactions

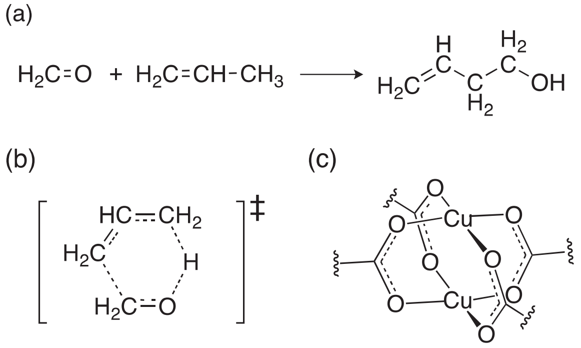
Lewis acid catalysis

If coordination sites of constituent metal ions of a MOF are coordinatively unsaturated, the MOF may function as a Lewis acid catalyst. QM/MM calculations have been applied to such Lewis acid catalysts.

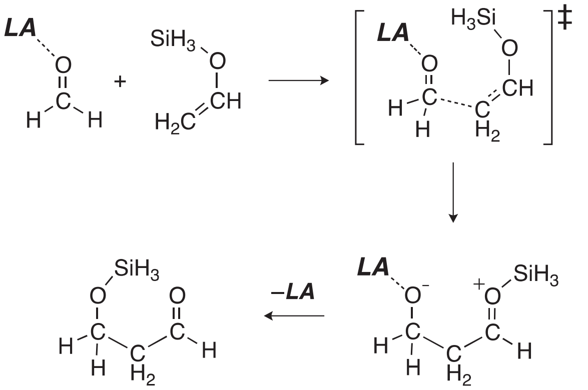
Choomwattana et al. studied the carbonyl-ene reaction between formaldehyde and propylene (Scheme 1a),[4] which may proceed via a six-membered transition state (Scheme 1b). They performed density functional theory (DFT) calculations on the uncatalyzed reaction and confirmed that the barrier for the reaction is very high (31.1 kcal/mol). However, QM/MM calculations at the ONIOM(B3LYP/6-31G(d,p):UFF) level showed that MOF-11 significantly decreases the barrier height to 24.1 kcal/mol. In this MOF-catalyzed reaction, an open Cu(II) center of the copper-paddlewheel (Cu-PDW) unit (Scheme 1c) within MOF-11 coordinates to the oxygen atom of formaldehyde, thereby facilitating the reaction.

Yadnum et al. studied the Mukaiyama aldol reaction between formaldehyde and silyl enol ether (Scheme 2) catalyzed by MOF-505 using the ONIOM(M06-L/6-311++G(2d,2p):UFF) method.[5] The LUMO energy level of formaldehyde is lowered upon its coordination to Cu-PDW. Thus, the energy gap between the LUMO of the aldehyde and the HOMO of the silyl enol ether is reduced, which leads to a significantly lower energy barrier for the MOF-catalyzed reaction.

One of the most attractive features of MOFs is the tunability of organic linkers, which allows MOFs to function as asymmetric catalysts.[6] For example, Tanaka et al. reported that the two-dimensional MOF (**1**; Fig. 1a) composed of Cu-PDW units and BINOL-type linkers catalyzed the asymmetric ring-opening (ARO) reaction of cyclohexene oxide with aniline, which yielded the (*R*,*R*)-isomer as the major product (Scheme 3).[7] The reaction exhibited rather poor reactivity and enantioselectivity when (*S*)-BINOL was used as the catalyst. These results suggested that the MOF exerts a significant influence on the enantioselectivity, and that the Lewis-acid Cu(II) site may play a key role in the catalysis.



Scheme 1. (a) Reaction between formaldehyde and propylene. (b) Transition state. (c) Cu-PDW.



Scheme 2. Lewis acid (LA) catalyzed Mukaiyama aldol reaction between formaldehyde and silyl enol ether.

Doitomi et al. performed QM/MM calculations on this reaction using the model shown in Fig. 1b and c.[8] The B3LYP-D3 method was used to describe the dispersion effect. UFF and UFF4MOF were used for the MM region. The calculations showed that the Cu(II) center in Cu-PDW can indeed act as a Lewis acid site for the ARO reaction. Another possibility was also examined in which the OH groups of the BINOL moiety play catalytic roles, but in this case, the barrier was higher than that for the reaction that uses Cu(II). For a reactant complex (RC) that may be formed first, four different structures—(*R*,*R*)-1-RC, (*R*,*R*)-2-RC, (*S*,*S*)-1-RC, and (*S*,*S*)-2-RC—were obtained. QM/MM reaction analyses showed that the (*R*,*R*)-isomer can be formed most favorably from (*R*,*R*)-2-RC, while the (*S*,*S*)-isomer can be formed from (*S*,*S*)-1-RC. Both of these pathways consist of two major steps (Fig. 2); namely, the ring-opening and proton-transfer steps. The first step has a higher barrier and thus determines the enantioselectivity. The (*R*,*R*)-2 pathway has a lower barrier than the (*S*,*S*)-1 pathway in the first step, consistent with the experimentally observed enantioselectivity. A close inspection of the transition states revealed that there were CH–π interactions in the lower-energy (*R*,*R*)-2 pathway ((*R*,*R*)-2-TS1, Fig. 3), whereas such interactions could not be found in the (*S*,*S*)-1 pathway. Thus, CH–π interactions can induce enantioselectivity in this particular MOF-catalyzed reaction. Similar mechanisms may also operate in other MOF-catalytic systems. The important role of CH–π interactions was further supported by another "control" computational experiment, in which the dispersion effect was intentionally turned off. Here, B3LYP/MM was used instead of B3LYP-D3/MM; consequently, the transition state in the (*R*,*R*)-2 pathway was not as stable as it was in the B3LYP-D3/MM calculations, indicating the important role of the CH–π interactions in stabilizing the (*R*,*R*)-2 pathway. These computational outcomes led to the hypothesis that the enantioselectivity should be improved if the energy gap between the transition states in the first step is increased. This may be done, for example, by attaching an electron-donating substituent to the naphthol moiety of the linker, thereby enhancing the CH-π interactions in the (*R*,*R*)-2 pathway. This hypothesis was supported by additional computational experiments.

Another interesting finding was the flexible nature of the Cu-PDW unit. It turns out that the originally symmetric Cu-PDW unit undergoes a significant geometric distortion during the ring-opening process. Specifically, one of the coordination bonds in the Cu-PDW unit is cleaved, thus resulting in detachment of a carboxylate ligand at the lowest-energy transition state ((*R*,*R*)-2-TS1, Fig. 4). The reason for this geometric distortion pertains to the formation of an anionic species. Thus, although the epoxide unit is initially neutral, as the ring-opening reaction progresses, an alkoxide anion

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