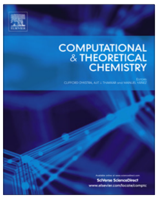
Computational and Theoretical Chemistry 1101 (2017) 36–45

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Evaluation of density functionals for elementary steps of selective oxidation reactions

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ARTICLE INFO

Article history:
Received 14 October 2016
Received in revised form 24 November 2016
Accepted 13 December 2016
Available online 18 December 2016

Keywords:
Redox reaction
Metal oxo complex
Density functional
Benchmark
CCSD(T) reference

ABSTRACT

Aiming at redox reactions involving metal oxides, we evaluated various approaches of Density Functional Theory regarding the energetics of 8 processes consisting of at least 3 elementary steps: 1 GGA functional, 1 meta-GGA functional, 6 GGA-based hybrid functionals, 3 hybrid meta-GGA functionals, as well as 1 double-hybrid functional. The tested reactions included hydrogenation processes of metal oxides, epoxidation and oxidative dehydrogenation of organic adsorbates at metal-oxo groups. The metal oxides were modeled by single-center oxidic complexes of V, Mo, and Bi. Using energies obtained at the CCSD(T) level as reference, we characterized the energetics of these processes by (i) absolute energies of intermediates, relative to the initial state of the process, and (ii) reaction energies of elementary steps. According to criterion (i), the results obtained with the hybrid functionals TPSSh, M06, and B3LYP, agree best with the reference; overall mean absolute deviations (OMAD) are 17–21 kJ mol^{-1}. An empirical correction for the dispersion interaction slightly improves the average energetics of TPSSh and B3LYP for adsorption and desorption processes. The meta-GGA functional M06L does quite well, OMAD = 25 kJ mol^{-1}, especially compared to the GGA functional PBE, OMAD = 37 kJ mol^{-1}, often used for processes at surfaces.

1. Introduction

The synthesis of about a quarter of all organic chemicals of industrial relevance involves a catalytic oxidation step [1]. Thus, the importance of selective oxidation catalysis for the chemical industry is easy to grasp. Such processes often require a metal oxide as catalyst, e.g., the SOHIO process that converts propylene to acrylonitrile during ammoxidation over Mo or Sb based catalysts [2,3]. In particular, reactions catalyzed by mixed metal oxides (MMO), i.e., oxide materials that contain centers of more than one metallic element, like the so-called Mitsubishi M1/M2 catalysts [4], are of growing interest [5].

Despite of various computational studies on this topic [6–9], the quantum chemical modeling of industrially relevant selective oxidation processes is still a non-trivial task [10]. Redox processes on insulating oxidic materials often involve the formation of reduced metal centers and, related to that, highly localized *d*- or *f*-states [11]. Such types of systems cannot be accurately described by semi-local DFT methods, commonly employed when one models reactions on solid surfaces using a plane-wave approach. These methods suffer to a notable extent from the self-interaction error [12–14] which is reflected by an artificially delocalized electron density at reduced metal centers and underestimated band (or HOMO-LUMO) gaps [15]. Such an erroneous description of the electronic structure translates into inaccurate energetics and ultimately leads to an unreliable representation of the reactivity.

Various studies addressing catalytic processes on oxide materials applied hybrid functionals instead of semi-local (LDA, GGA) functionals [6–8,16–22]. Yet, DFT calculations with GGA functionals can still be an economic choice if corrected, at least in part, for the self-interaction error. A popular approach for periodic models of extended systems using a plane wave basis set is the DFT+U scheme which improves the description of *d*- and *f*-electrons by the addition of an "on-site" potential [23,24]. An advantage of this approach is the relatively low computational cost. Yet, determining the parameters for the on-site potential, that provides a sufficiently adequate description for all reaction intermediates, is a non-trivial task and sometimes even impossible [9,10]. Alternatively, as mentioned, one may invoke a hybrid functional that, at least in part, accounts for the self-interaction error by an admixture of exact exchange (EEX) [25]. Hybrid functionals are superior to standard GGA functionals for describing reducible oxidic systems

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http://dx.doi.org/10.1016/j.comptc.2016.12.021

[11,26,27]. However, results of hybrid functionals still have to be considered with care [10]. Studies on the oxidation of alkanes over VO_x catalysts indicated a discrepancy of up to 60 kJ mol^{-1} between reaction barriers from B3LYP hybrid DFT and CCSD(T) calculations [16]. Another drawback of hybrid functionals is the increased computational demand, especially for periodic calculations. Thus, presently, hybrid functionals can only routinely be used in combination with finite molecular models.

Hybrid functionals come in a variety of flavors, differing notably in the amount of EEX incorporated. Therefore, it seems prudent to evaluate how well the various hybrid functionals describe redox processes on oxidic materials, as done in an earlier work addressing perovskites [28]. In that study, the functionals PBE0 and HSE have been determined as most accurate [28]. The present work aims at benchmarking the performance of selected hybrid functionals for modeling molecular processes relevant to oxidation catalysis over metal oxides to get a rough estimate of the accuracy that can be achieved by calculations with hybrid functionals. To this end, we selected 6 hybrid functionals (B3LYP, ωB97X, ωB97XD, PBE0, HSE06, BHandH) with EEX contributions from 10% to 50%, as well as the pure GGA functional PBE, the meta-GGA functional M06L, the hybrid meta-GGA functionals TPSSh, M06, and M06-2X, 10–54% EEX, as well as the double-hybrid functional B2-PLYP with 53% EEX. The set of test reactions included the hydrogenation of oxide cluster models of V, Mo, and Bi, as well as epoxidation and oxidative dehydrogenation reactions at oxidic clusters of V and Mo. The choice of the metals was motivated by the fact that these elements are often used in catalysts for oxidation reactions, e.g. $BiMoO_x$ or $MoVTeNbO_x$ for the selective oxidation of small alkanes [10].

We evaluated the quality of DFT calculations by comparing them to the corresponding results obtained at the CCSD(T) level, focusing primarily on the absolute stability of intermediate species with respect to the corresponding initial state. We also compared reaction energies of elementary steps. Although quite large systems can nowadays be treated by CCSD(T) calculations of molecular systems [29,30], we deliberately chose molecular model systems with one metal center for their relative ease of interpretation.

2. Computational models and methods

2.1. Cluster models and model reactions

The model reactions selected for the present benchmark study are hydrogenation processes of metal oxo complexes (Scheme 1), the transfer of an oxo group from oxidized metal centers to an olefin yielding an epoxide (epoxidation, Scheme 2), and the oxidative dehydrogenation (ODH) of an alkane over a metal oxo group (Scheme 3). For the first type of reactions, we considered adding H atoms at a metal oxo group, addressing three elementary steps (Scheme 1): (i) addition of a hydrogen atom to an oxo group M═O yielding a hydroxyl group, M—OH, (ii) addition of a second H atom to the hydroxyl group to form a water molecule, $M{-}OH_2$, and (iii) the subsequent elimination of the water molecule, leaving behind an empty coordination site M—□ at the metal center. We examined oxide clusters of V, Mo, and Bi, with special emphasis on vanadium oxide. We started with the cluster model $(HO)_3V{=}O$ to represent an active center of VO_x-based catalysts (Reaction 1, Scheme 1). If a water molecule is eliminated from a layered VO_x material like V_2O_5, an O center of the layer underneath, that initially interacts mainly via dispersive interaction with the layer above, may ultimately coordinate to the reacting V center during the removal of the water molecule [31]. In an attempt of representing this structural aspect, we also considered the model complex $(H_2O)(HO)_3V{=}O$ with an additional aqua moiety at the V center (Reaction 2, Scheme 1). Furthermore, we considered the model $(H_2O)(HO)_2V{=}O$ with a reduced V^{+4} center (Reaction 3, Scheme 1). To explore analogous hydrogenation reactions with other metal oxo complexes, like those of the transition metal Mo as well as of the *p*-block metal Bi, we constructed two additional models. Similar to the model $(HO)_3V{=}O$ for Reaction 1, these models were chosen to be neutral and to feature a four-fold coordinated metal center in its highest oxidation state: (i) $(HO)_2Mo^{+6}({=}O)_2$ (Reaction 4, Scheme 1), and (ii) $(HO)_3Bi^{+5}{=}O$ (Reaction 5, Scheme 1). Similar models had been used in previous computational studies [21,22].

In addition to these five hydrogenation reactions, we considered two epoxidation reactions, and one ODH reaction. One of the reactions involves the epoxidation of ethylene at $[(H_3PO)(O_2)_2Mo{=}O]$ via a concerted non-radical pathway (Reaction 6, Scheme 2) [32]. The remaining two reactions at $(HO)_3V{=}O$, the epoxidation of ethylene (Reaction 7, Scheme 2) and the ODH of ethane, yielding ethylene and water (Reaction 8, Scheme 3), are assumed to follow a radical pathway.

2.2. Computational methods

The DFT calculations were carried out with the software package Gaussian 09 [33], unless specified differently. For systems with unpaired electrons, we used the spin-unrestricted Kohn-Sham (UKS) approach. The functionals considered in this study include the GGA functional PBE [34], and the meta-GGA functional M06L [35] (which do not incorporate any exact exchange) as well as the hybrid meta-GGA functionals TPSSh (10% EEX) [36], M06 (27%) [37], and M06-2X (54%) [37], the double-hybrid functional B2-PLYP (53% EEX) [38], as well as the hybrid functionals B3LYP (20%) [39], ωB97XD (22%) [40], ωB97X (22%) [40], PBE0 (25%) [41], HSE0 (25%) [42], and BHandH (50%) [25]. To simplify the following discussion, we will sometimes refer to the last three groups collectively as "hybrid functionals".

For V, Mo, and Bi, we employed Stuttgart–Dresden effective core potentials (ECP) and the corresponding basis sets [43–45]; the ECPs represent 10 core electrons of V, 28 core electrons of Mo, and 60 core electrons of Bi. When combined with the all-electron 6-31G(*d*,*p*) basis set for the atoms H, O, and C [46], we refer to these basis sets as BS1. We optimized the structures of reactants, intermediates, and products with BS1, without symmetry restrictions, using the functional PBE0, and we confirmed all structures by a normal mode analysis. Subsequently, for all functionals and the reference energies at the CCSD(T) level, we applied more flexible basis sets, labeled as BS2, in single-point fashion at structures obtained at the PBE0/BS1 level. Geometries optimized at the PBE0 level of theory were chosen for consistency with an earlier model study [31]. Basis set BS2 comprised the augmented correlation-consistent triple-zeta basis, aug-cc-pVTZ, on H, C, O, and V [47]; on Mo and Bi we kept the same ECPs and the corresponding basis sets as in BS1. We determined charges based on the NBO scheme as implemented in Gaussian09 using BS2 [48]. The results for the double-hybrid functional B2-PLYP were obtained using the program package Orca 3.0.2 [49].

To account for the effect of dispersion interactions, which are not well described within most exchange-correlation approximations, we applied the empirical D3 scheme [50] with BJ damping [51] as implemented in the program Turbomole 6.6 [52], to the functionals performing best in our study, TPSSh and B3LYP. The third successful functional, M06, aims at directly representing the effect of dispersion interactions [53,37]. The pair of functionals ωB97X and ωB97XD provides another opportunity for exploring the effect of dispersion forces on the energetics of the redox processes under study. Note that the functional ωB97XD can be viewed as a modification of the functional ωB97X to account for dispersive interactions [40].