



Effects of van der Waals density functional corrections on trends in furfural adsorption and hydrogenation on close-packed transition metal surfaces



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ARTICLE INFO

Article history:

Received 14 November 2013

Accepted 2 December 2013

Available online 16 December 2013

Keywords:

Furfural hydrogenation

Periodic Density Functional Theory

Van der Waals density functional

Linear scaling relationship

Brønsted–Evans–Polanyi relationship

ABSTRACT

The hydrogenation of furfural to furfuryl alcohol on Pd(111), Cu(111) and Pt(111) is studied with both standard Density Functional Theory (DFT)-GGA functionals and with van der Waals-corrected density functionals. VdW-DF functionals, including optPBE, optB88, optB86b, and Grimme's method, are used to optimize the adsorption configurations of furfural, furfuryl alcohol, and related intermediates resulting from hydrogenation of furfural, and the results are compared to corresponding values determined with GGA functionals, including PW91 and PBE. On Pd(111) and Pt(111), the adsorption geometries of the intermediates are not noticeably different between the two classes of functionals, while on Cu(111), modest changes are seen in both the perpendicular distance and the orientation of the aromatic ring with respect to the planar surface. In general, the binding energies increase substantially in magnitude as a result of van der Waals contributions on all metals. In contrast, however, dispersion effects on the kinetics of hydrogenation are relatively small. It is found that activation barriers are not significantly affected by the inclusion of dispersion effects, and a Brønsted–Evans–Polanyi relationship developed solely from PW91 calculations on Pd(111) is capable of describing corresponding results on Cu(111) and Pt(111), even when the dispersion effects are included. Finally, the reaction energies and barriers derived from the dispersion-corrected and pure GGA calculations are used to plot simple potential energy profiles for furfural hydrogenation to furfuryl alcohol on the three considered metals, and an approximately constant downshift of the energetics due to the dispersion corrections is observed.

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1. Introduction

Furfural is central to a variety of catalytic processes associated with biomass chemistry. It can be directly derived from biomass sources and can be further converted to useful chemicals and fuels via hydrogenation and hydrodeoxygenation (HDO). In this context, a model reaction that has received significant attention is the hydrogenation of furfural to furfuryl alcohol [1–8]. In spite of a substantial amount of study, however, furfural hydrogenation catalysts, most of which are based on transition metals or metal alloys, are still incompletely understood, and the hydrogenation process remains the subject of a significant amount of research [2,7,9–11]. As is the case for numerous other hydrogenation chemistries, such as the selective hydrogenation of acetylene [12], the key catalytic imperative is to maintain a balanced reaction activity and selectivity. This task is particularly challenging in the

case of furfural, however, given the presence of multiple conjugated bonds and oxygen-containing functional groups.

Density Functional Theory (DFT) calculations have, in recent years, become standard tools to explore heterogeneous catalytic reaction pathways and related thermodynamic and kinetic properties [13–15]. In particular, when coupled with correlations such as Brønsted–Evans–Polanyi (BEP) relationships and scaling relationships, DFT calculations are extremely powerful for screening, evaluating, and predicting the catalytic properties of a wide range of systems [16–18]. Nevertheless, DFT calculations using the standard Generalized Gradient Approximation (GGA) may be insufficient to accurately describe the weak dispersion effects associated with van der Waals interactions [19], and this problem is especially apparent in the adsorption of highly conjugated organic compounds on precious metals. For example, the adsorption energy of pyridine on Au(111) is underestimated using PW91 or PBE functionals although these functionals provide reasonable descriptions of adsorbate configurations [20]. An additional example is provided by the work of Bilić et al., who showed, using DFT and CASSCF calculations, that on copper, silver and gold surfaces, the magnitudes of the binding

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energies of benzene adsorption are significantly underestimated when dispersion effects are neglected [21].

Recent theoretical developments have provided means to partially address the above problems by correcting the total energies from GGA calculations through addition of contributions from non-local density functionals [22–25]. Using DFT calculations and semiempirical corrections based on a QM/MM approach, Tonigold et al. were able to determine adsorption energies of benzene and pyridine in good agreement with experiments on Au(111) [26]. Calculations using the PBE-D3 method of dispersion correction have also been extended recently to mechanistic studies of furfural conversion on Pd [27]. In spite of these advances, however, trends-based analyses that focus on how dispersion forces impact the thermochemistry and kinetics of surface reactions are still relatively rare, and this contribution seeks to provide such trends for the specific case of furfural hydrogenation.

We report on periodic DFT calculations of adsorption energies, adsorbate geometries, and hydrogenation barriers associated with furfural hydrogenation using several vdW-DF functionals, including optPBE, optB88, optB86b, as well as Grimme's method. Results are given for Pd(111), Pt(111), and Cu(111) surfaces, and the impact of the dispersion corrections, as compared to GGA (PW91 and PBE) results, on the energetics and geometries is described. A simple correlation to permit more rapid estimation of furfural adsorption energetics in these and related systems is presented, and finally, a unified Brønsted–Evans–Polanyi relationship for the PW91 and optB86b functionals is developed.

2. Computational methods

Periodic DFT calculations are performed using the Vienna Ab initio Simulation Package (VASP 5.2) [28,29], where the ionic cores are described by the projector augmented wave (PAW) method [30,31]. The Kohn–Sham valence states are expanded with plane wave basis sets up to 340 eV. The self-consistent iteration is converged up to 1×10^{-6} . The ionic step is converged when the force on each atom is less than 0.02 eV/Å. The Methfessel–Paxton smearing scheme is used [32], with a Fermi population of the Kohn–Sham states at $k_B T = 0.2$ eV. The total energies are then extrapolated to 0 K.

Several functionals in the vdW-DF family are used in this study, including vdW-DF functionals, such as optPBE, optB88 [23], and optB86b [33], developed by Klimes et al., where the dispersion correlations depend on the density functional in the form of non-local correlation terms. We have also performed some tests using Grimme's PBE-D2/D3 method [25], which relies on predetermined C_6 coefficients, on Pd and Cu surfaces. The PBE-D2 method is used to optimize bulk lattice constants and structures of adsorbed configurations of furfural and furfuryl alcohol, while single point calculations with the PBE-D3 method are used to calculate the binding energies based on both these geometries and geometries optimized with the PBE-GGA [35] functional (bulk cohesive energies are evaluated with PBE-D2 only). In addition to PBE, the standard GGA-PW91 [34] functional is also employed. The reaction barriers for BEP relationship development are calculated using PW91 and optB86b functionals, which we take to be generally representative of the non-dispersion and dispersion correction cases, respectively.

A three-layer, $p(4 \times 4)$ slab, which is sufficiently large to minimize the lateral interactions of adsorbates and their periodic images, is used as the surface model. Adsorption is allowed on only one side of the slab, corresponding to a surface coverage of 1/16 ML. The top layer of the slab is allowed to relax, while the bottom layers are fixed at the appropriate bulk lattice constant. A vacuum spacing equivalent to at least five metal layers is used between any successive metal slabs. For Pd, Cu and Pt bulk relaxations, a $16 \times 16 \times 16$ Monkhorst–Pack k -point mesh is employed [36]. The surface Brillouin zone is sampled with a $2 \times 2 \times 1$ k -point mesh for Pd and Pt, and a $4 \times 4 \times 1$ k -point mesh for Cu. Based on these parameters, we estimate that the binding energies in this paper have converged to within 50 meV. The total energies of relevant gas phase species are calculated using the same functionals

in a box with dimensions of $25 \times 26 \times 27$ Å; the gamma-point is used for these calculations, with a Gaussian smearing parameter of 0.01 eV. Spin polarization is used for all gas phase calculations and for surface-adsorbed species with unpaired electrons. Dipole corrections are included in all calculations.

Energy barriers are calculated using the Climbing Image Nudged Elastic Band (CINEB) [37,38] method on three-layer slabs (top layer relaxed) [39,40]. The dimer method is then used to further refine the TS's obtained from the CINEB calculations. Each transition state has been confirmed to have only one imaginary (negative) vibrational mode.

3. Results and discussion

3.1. Bulk properties of Pd, Cu, and Pt

Bulk lattice constants have been optimized for each DFT functional in a four-atom fcc cell; the resulting values are listed in Table 1. The PW91 and PBE functionals overestimate the lattice parameters for both Pd and Pt. The lattice parameters are generally slightly smaller with vdW-DF functionals, giving better agreement with experimental values [41]. Overall, optB88 and optB86b perform modestly better than the other functionals. We note that the calculated lattice parameters using vdW-DF functionals in this study are in good agreement with the theoretical values reported by Klimes et al. [33]. The bulk lattice constants (for Pd and Cu) optimized with the PBE-D2 method are also in good agreement with the experimental value compared with the GGA functionals.

The cohesive energies are calculated as $E_{\text{coh}} = E_{\text{atom}} - E_{\text{bulk}}/4$. For Pd, the PW91 and PBE functionals are able to predict the cohesive energies to within 0.2 eV of the experimental values. The agreement with experiment is generally good for optPBE, optB88, and optB86b. The cohesive energies predicted by the PBE-D2 method are larger than the experimental values by approximately 0.5 eV for Pd and Cu.

3.2. Thermochemistry of hydrogenation intermediates

We begin by describing the calculated geometries of furfural and furfuryl alcohol in the gas phase and on Pd(111), Pt(111), and Cu(111). We then briefly summarize corresponding results for adsorption of other intermediates resulting from furfural hydrogenation. Finally, we present a simple, bond order-based scaling relationship that provides a useful framework for interpreting and extrapolating the calculated adsorption energies of furfural hydrogenation intermediates.

3.2.1. Geometries of gas phase furfural and furfuryl alcohol

Fig. 1 illustrates the calculated gas phase geometries of furfural and furfuryl alcohol, including both *cis* and *trans* configurations. The optimized structures, obtained with all of the DFT functionals, are given in the Supporting Information, where it is seen that the *trans* configuration is, in all cases, more energetically favored by approximately 0.03–0.05 eV. This result is consistent with the fact that the *trans* configuration has been observed in IR and Raman spectroscopy studies [42].

Table 1

Lattice parameters (in Å) and cohesive energies (in eV) of bulk Pd, Pt, and Cu from PW91, PBE, optPBE, optB88, optB86b, and PBE-D2 functionals.

GGA functionals	Lattice constant			Cohesive energy		
	Pd	Pt	Cu	Pd	Pt	Cu
PW91	3.95	3.99	3.64	3.76	6.87	3.54
PBE	3.95	3.98	3.60	3.74	6.61	3.49
<i>vdW-DF functionals</i>						
optPBE	3.97	3.97	3.65	3.78	5.58	3.44
optB88	3.94	3.96	3.62	4.03	5.83	3.60
optB86b	3.91	3.93	3.60	4.24	6.14	3.79
PBE-D2	3.91	–	3.57	4.37	–	3.92
Expt.[41]	3.89	3.92	3.61	3.89	5.84	3.49

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