Journal of Catalysis 321 (2015) 39–50

Contents lists available at ScienceDirect

Journal of Catalysis

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

Theoretical investigation of the reaction mechanism of the hydrodeoxygenation of guaiacol over a Ru(0001) model surface

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A R T I C L E   I N F O

Article history:
Received 31 July 2014
Revised 23 October 2014
Accepted 1 November 2014
Available online 24 November 2014

Keywords:
Guaiacol
Ruthenium
Density functional theory
Microkinetic modeling
Deoxygenation
Hydrodeoxygenation
Lignin

A B S T R A C T

The reaction mechanism of the hydrodeoxygenation of guaiacol to aromatic products has been studied by density functional theory calculations and microkinetic modeling over a Ru(0001) model surface. Our model suggests that the dominant hydrodeoxygenation pathway proceeds via O–H bond cleavage of guaiacol, $C_6H_4(OH)(OCH_3)$, to $C_6H_4(O)(OCH_3)$, followed by dehydrogenation of the methoxy group to $C_6H_4(O)(OC)$, decarbonylation to C_6H_4O, and finally hydrogenation to phenol. At the adsorbed $C_6H_4(O)(OCH)$ intermediate, a competitive deoxygenation pathway is identified, which involves methyne group removal to $C_6H_4O_2$, followed by hydrogenation to $C_6H_4(OH)(O)$, dehydroxylation to C_6H_4O, and finally hydrogenation to phenol. In agreement with experimental results, phenol is predicted to be the major product and catechol is the most relevant minority side product. Further deoxygenation of phenol to benzene is found to be slow. Finally, computations predict the last dehydrogenation step of the methoxy species in guaiacol to be at least partially rate controlling over Ru(0001).

1. Introduction

With the continued depletion of fossil resources as a source for fuels and chemicals, renewable raw materials such as biomass have drawn more and more attention as a possible source for fuels and chemicals. Bio-oils produced from fast pyrolysis and hydrothermal liquefaction of lignocellulosic biomass have been identified as a promising alternative feedstock for fuels and chemical production with several environmental advantages. For example, bio-oil production is CO_2 neutral and its conversion emits no SO_x and 50% less of NO_x than diesel oil combustion in a gas turbine [1]. The composition of bio-oils depends heavily on the type of biomass and the production conditions, but bio-oils are generally a complex mixture of water (15–30%) and many organic compounds, including organic acids, aldehydes, alcohols, esters, phenol derivatives (50–65%), and lignin-derived oligomers (20%) [2,3]. A disadvantage of bio-oils is their high viscosity, high corrosiveness (acidity), instability, and low heating value, *etc.*, originating from the high oxygen content of most bio-oils. Therefore, upgrading of bio-oils, that is, deoxygenation, is critical for its application as a liquid fuel or chemical feedstock.

Catalytic upgrading of bio-oils is commonly done by hydrodeoxygenation (HDO), which involves the challenging C–O bond cleavage reaction. Since bio-oils are a mixture of hundreds of compounds, the only viable strategy for better understanding the catalytic upgrading process involves the mechanistic investigation of model compounds. Guaiacol ($C_6H_4(OH)(OCH_3)$) is such a representative compound of phenol derivatives and lignin-derived oligomers since it contains one phenyl ring and two oxygen-containing functional groups, –OH and $-OCH_3$. A considerable number of papers have reported experimental investigations on the catalytic hydrodeoxygenation of guaiacol on transition metals such as Fe [4,5], Ru [5–7], Rh [7–9], Pd [5,7,8], Pt [5,7,8,10], and bimetallic catalysts such as Co–Mo [11], Pt–Sn [12], Ni–Cu [13], Rh–Pt [8], and Pd–Fe [5]. Nimmanwudipong and coworkers [10] have mapped a reaction network for the hydrodeoxygenation of guaiacol over Pt/γ-Al_2O_3 in the presence of H_2 based on selectivity-conversion data, which is very insightful but lacks straightforward evidence. Sun and coworkers [5] have also proposed on the basis of their products a possible reaction pathway for Ru, Pd, and Pt catalysts, guaiacol → catechol → phenol → benzene and a different one, guaiacol → phenol → benzene, for Fe and Pd–Fe catalysts.

In this study, we aimed at identifying the reaction mechanism and possible activity descriptors for the HDO of guaiacol over Ru(0001) model surfaces using density functional theory calculations and mean-field microkinetic modeling. To the best of the authors' knowledge, no theoretical study on the catalytic hydrodeoxygenation of guaiacol over transition metal catalysts has yet been published.

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http://dx.doi.org/10.1016/j.jcat.2014.11.003
0021-9517/

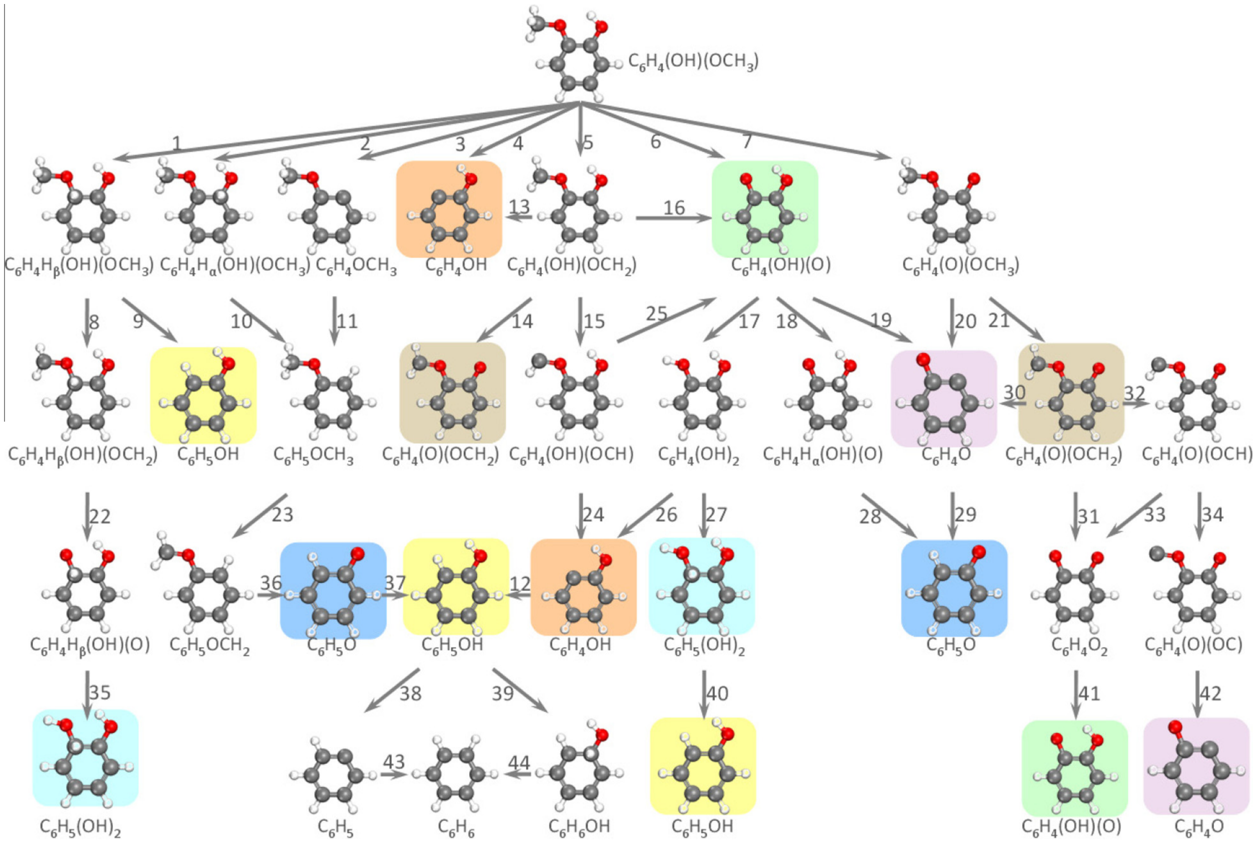

Fig. 1. Reaction network investigated for the hydrodeoxygenation of guaiacol to aromatic products over Ru(0001). For clarity, duplicate structures are highlighted by identical background colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Methods

All calculations presented in this work were performed using the periodic DFT implementation in the Vienna Ab Initio Simulation Package (VASP) [14,15]. The electron–ion interactions were described by the projector-augmented wave (PAW) method. The PAW method is a frozen-core all-electron method that uses the exact shape of the valence wave functions instead of pseudo-wave functions [16]. The exchange correlation energy has been calculated within the generalized gradient approximation (GGA) using the PBE functional form [17,18]. For dispersion interactions, we used the DFT-D3 methodology [19]. An energy cutoff for plane waves of 400 eV was employed throughout this study.

The total energy of HCP-Ru bulk approaches a minimum when its lattice constants are $a = 2.7020$ Å and $c = 4.2741$ Å, which is in reasonable agreement with the experimental values ($a = 2.7059$ Å and $c = 4.2815$ Å [20]). The Ru(0001) surface was constructed as a periodic slab with four Ru layers separated by a vacuum layer of 15 Å in order to eliminate interactions between the slab and its images. Each Ru layer had 16 Pd atoms with a $(4 \times 2\sqrt{3})$ periodicity, allowing for adsorbate coverages as low as 1/16 ML. The bottom two Ru layers were fixed to their optimized bulk configuration during all computations, while the top two layers were fully relaxed. The adsorbates were free to relax in all directions. All atomic coordinates of the adsorbates and the Ru atoms in the relaxed layers were optimized to a force less than 0.03 eV/Å on each atom. All self-consistent field (SCF) calculations were converged to 1×10^{-3} kJ/mol. Brillouin zone integration was performed using a $4 \times 4 \times 1$ Monkhorst–Pack grid and a Methfessel–Paxton smearing of 0.2 eV. In all cases, the convergence of total energy with respect to the *k*-point mesh and with respect to plane-wave energy cutoff has been confirmed. The convergence criterion for the total energy was set to 10^{-7} eV.

Adsorption energies of all the surface intermediates reported in this paper were calculated in their most favorable adsorption modes. The adsorption energies, E_{ads}, were calculated by the following equation:

$$E_{\text{ads}} = E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate(gas)}} \quad (1)$$

where $E_{\text{slab+adsorbate}}$ is the total energy of an adsorbate bound to the Ru slab, E_{slab} is the total energy of the clean Ru slab, and $E_{\text{adsorbate(gas)}}$ is the total energy of the adsorbate in the gas phase.

Finally, transition states for elementary reaction steps were determined by a combination of the nudged elastic band (NEB) method [21] and the dimer method [22–24]. In the NEB method, the path between the reactant and product is discretized into a series of structural images. The image that is closest to a likely transition state structure was then employed as an initial guess structure for the dimer method. All adsorption energies and activation barriers reported in this study have been zero-point corrected (ΔZPE).

For the microkinetic modeling, we have employed the same methodology as described in our previous paper [25]. The nonlinear steady state surface species equations have been solved using the BzzMath library [26] developed by Buzzi-Ferraris.

3. Results and discussion

Fig. 1 illustrates the reaction pathways included for the HDO of guaiacol to benzene over the Ru(0001) surface model. In the following, we will first discuss the effects of dispersion corrections