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Full Length Article

Hydrogenation of *o*-cresol on platinum catalyst: Catalytic experiments and first-principles calculations

Yaping Li[a], Zhimin Liu[b], Wenhua Xue[a], Steven P. Crossley[b], Friederike C. Jentoft[b,1], Sanwu Wang[a,*]

[a] *Department of Physics and Engineering Physics, The University of Tulsa, Tulsa, OK 74104, USA*
[b] *School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA*

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ABSTRACT

Catalytic experiments were performed for the hydrogenation of *o*-cresol in *n*-dodecane over a platinum catalyst. Batch reactions analyzed with an *in-situ* ATR IR probe suggest that the hydrogenation results in the formation of the final product, 2-methyl-cyclohexanol, with 2-methyl-cyclohexanone as the intermediate product. *Ab initio* density-functional theory was employed to investigate the atomic-scale mechanism of *o*-cresol hydrogenation on the Pt(111) surface. The formation of 2-methyl-cyclohexanone was found to involve two steps. The first step is a hydrogen abstraction, that is, the H atom in the hydroxyl group migrates to the Pt surface. The second step is hydrogenation, that is, the pre-existing H atoms on Pt react with the carbon atoms in the aromatic ring. On the other hand, 2-methyl-cyclohexanonol may be produced through two paths, with activation energies slightly greater than that for the formation of 2-methyl-cyclohexanone. One path involves direct hydrogenation of the aromatic ring. Another path involves three steps, with the partial hydrogenation of the ring as the first step, hydrogen abstraction of the —OH group as the second, and hydrogenation of remaining C atoms and the O atom the last.

1. Introduction

Biofuels derived from lignocellulosic biomass have received significant attention lately due to environmental concerns and increasing needs of energy supply [1–7]. Lignin-derived phenolics such as phenols, cresols and guaiacols are important components of crude bio-oil [8,9], but require upgrading prior to use [10]. Extensive research has been conducted for the conversion of phenolics to increase the stability of bio-oil and produce transportation fuels. The strong phenolic OH bond makes phenols and cresols, perhaps the most challenging biomass derived monomers to be deoxygenated. This has led to significant research efforts focused on the upgrading of phenolic compounds for improving the properties of bio-oils [11–17].

Cresol is a phenolic compound that has three isomers: *ortho*-cresol (*o*-cresol), *meta*-cresol (*m*-cresol), and *para*-cresol (*p*-cresol). Hydrogenation and hydrodeoxygenation of these three cresols were experimentally studied with various catalysts [18–25]. As early as 1967, it was demonstrated that hydrogenation of cresols with a rhodium catalyst generated methyl-cyclohexanols at the mild reaction temperature of 353 K, but *o*-cresol was found to yield a significant amount of the ketone intermediate, 2-methyl-cyclohexanone [18]. Hichri et al. studied hydrogenation of *o*-cresol on Ni/SiO_2 in isopropanol at the reaction temperatures of 393–413 K. They found that 2-methyl-cyclohexanol was the final product, but little 2-methyl-cyclohexanone was reported during the catalytic reaction [19]. Also using a Ni/SiO_2 catalyst, Shin and Keane [20] found that, at 473 K, cresol conversion produced both methyl-cyclohexanols and methyl-cyclohexanones with the latter as the intermediate products. Toluene was reported at more severe conditions of 573 K along with methyl-cyclohexanols and methyl-cyclohexanones. Other investigations have reported similar behavior [21–23]. For example, hydrodeoxygenation of *o*-, *m*-, and *p*-cresols on sulfided CoO-MoO/γ-Al_2O_3 (in hexadecane) at 498–673 K resulted in toluene and methyl-cyclohexane as the major products [21]. More recently, Nie et al. reported that the dominant product of selective conversion of *m*-cresol over bimetallic Ni-Fe catalysts at 573 K was toluene [23]. Similar observations were made by Zanuttini et al. for hydrodeoxygenation of *m*-cresol at 573 K with Pt supported on acidic supports [24]. On the other hand, at a relatively lower temperature (453 K), both hydrogenation and

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[*] Corresponding author.
E-mail address: sanwu-wang@utulsa.edu (S. Wang).
[1] Present address: Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA.

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hydrodeoxygenation of cresols were observed (over Pt/Beta zeolite in isooctane) [25].

In the last several years, a number of groups have reported their theoretical investigations for the catalytic conversions of phenol, guaiacol, and *m*-cresol on metal catalysts [11–15,23,26,27]. In particular, Nie et al. reported their calculations for determining the structure of *m*-cresol on several Ni, Fe, and NiFe surfaces [23] while Tan et al. reported their theoretical studies for the hydrodeoxygenation of *m*-cresol over platinum and ruthenium catalysts [27]. The atomic-scale mechanism of hydrogenation of *o*-cresol and *p*-cresol was not investigated, however. In this paper, we report results of a combination of an experimental work and *ab initio* calculations based on density-functional theory (DFT) for catalytic hydrogenation of *o*-cresol with platinum as the catalyst. In particular, we provide detailed data for energetics and reaction pathways, which are used to elucidate the reaction mechanisms at the atomic-scale.

2. Experimental and computational methods

2.1. Materials

o-cresol (99%), 2-methyl-cyclohexanone (≥99.5%), and *n*-dodecane (≥99%) were obtained from Sigma Aldrich Company. All chemicals were used without further purification. Platinum on carbon (5 wt.% loading, 205931-Aldrich) was used as catalyst.

2.2. Catalytic tests

The catalytic experiments were conducted in batch mode in a custom design Parr reactor of 300 ml volume. Quantitative analysis of the composition of the reaction mixture was performed by attenuated total reflection (ATR) IR spectroscopy. A Mettler-Toledo Sentinel^{TM} DiComp^{TM} High Pressure ATR–IR probe was connected to a ReactIR^{TM} iC10 module with a K4 conduit. The ATR-IR probe was integrated into the reactor side wall to avoid settling of catalyst particles into the cavity of the probe, right above the crystal. The lid of the reactor was equipped with a pressure transducer. In typical experiments, 120 ml of solvent and 25 mg of catalyst were charged into the reactor. The reactor was then purged five times with H_2. Subsequently, the reactor was pressurized with 200 psi H_2 and heated from room temperature to the reaction temperature of 408 K and kept at this temperature for 10 min before the IR background was collected. The reaction was started by injection of the reactant (*o*-cresol). IR spectra were collected every 30 s in the first 2 h and every 1 min in the following several hours.

2.3. *Ab initio calculations*

Ab initio calculations were based on density functional theory, the projector augmented wave (PAW) method, and plane-wave basis sets [28–37]. All the calculations were performed with the use of Vienna *ab initio* simulation package (the VASP code) [28–30]. The functionals within generalized gradient approximations, developed by Perdew, Burke, and Ernzerhof (PBE), were used to describe the exchange and correlation effects [32]. The Pt(111) surface was represented by a repeated supercell that contains a slab of Pt atoms and a vacuum region of 18 Å in height, as shown in Fig. 1. The slab consists of five metal layers with each layer containing 25 platinum atoms in the supercell (a 5 × 5 surface unit cell). The Pt atoms were initially located at their bulk positions with the bulk lattice constant determined by our calculations. In order to calculate the adsorption of a molecule, the molecule was initially placed on the top of the Pt slab (at various positions near the surface). Each configuration was then optimized *via* a conjugate-gradient technique using the total energy and the Hellmann-Feynman forces on the atoms [33]. For all the optimization calculations, the Pt atoms of the bottom two layers were fixed while the Pt atoms of the top three layers and all the atoms of the molecule were allowed to move until the forces on all the atoms that were allowed to relax were less than 0.05 eV/Å. The van der Waals (vdW) correction proposed by Tkatchenko and Scheffler [38] was added to the conventional DFT for determining adsorption geometries and energies. Reaction pathways and the associated barriers were determined with the conventional DFT using the climbing image nudged elastic band method [39,40]. A plane-wave energy cutoff of 400 eV and two special ***k*** points in the irreducible part of the two-dimensional Brillouin zone of the 5 × 5 surface cell were used for all the calculations.

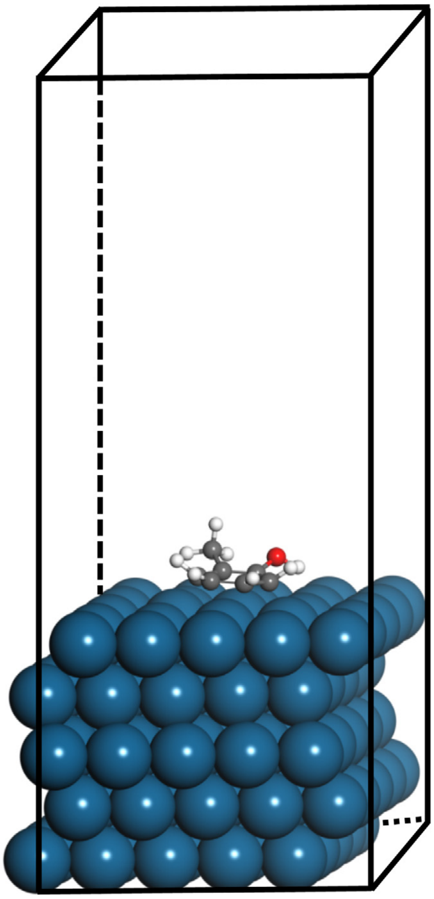

Fig. 1. Schematics of the supercell model for adsorption of *o*-cresol on the Pt(111) surface.

3. Results and discussion

The hydrogenation of *o*-cresol in the batch phase as monitored *via in-situ* ATR-IR spectra over Pt/C in dodecane reveals 2-methyl-cyclohexanone as an intermediate product as shown in Fig. 2. The intermediate is indicated by the appearance of IR band at 1723 cm^{-1}, which is assigned to the C═O vibration of 2-methyl-cyclohexanone. This product is also confirmed by GC–MS analysis of the liquid mixture. In order to obtain the concentration profiles of *o*-cresol and its hydrogenation products, calibrations based on the Lambert–Beer Law were performed by ATR-IR with specific IR bands of *o*-cresol (1253 cm^{-1}), 2-methyl-cyclohexanone (1723 cm^{-1}) and 2-methyl-cyclohexanol (976 cm^{-1}). Based on the concentration profiles, the selectivity of 2-methyl-cyclohexanone and 2-methyl-cyclohexanol were very close in the first 30 min 2-methyl-cyclohexanone reached a maximum concentration after 50 min when the conversion of *o*-cresol was about ca. 65%. After that