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Theoretical and experimental studies of the adsorption geometry and reaction pathways of furfural over FeNi bimetallic model surfaces and supported catalysts

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ABSTRACT

Controlling the activity and selectivity of hydrodeoxygenation (HDO) of biomass-derivatives is critical for the utilization of biomass as renewable sources for chemicals and fuels. Furfural, produced by the hydrolysis and dehydration of xylose from hemicellulose, is a promising biomass-derivative to produce important biofuels like 2-methylfuran. Using a combination of density functional theory (DFT) calculations and surface science measurements on Fe/Ni(1 1 1) model surfaces, our results indicate that furfural bonds to the bimetallic surfaces primarily through the C=O bond with the furan ring tilted away from the surface, leading to the production of 2-methylfuran through the HDO reaction with furfuryl alcohol being identified as the likely intermediate. Similar preferential interaction of the C=O group over the furan ring is also confirmed on SiO_2-supported FeNi bimetallic catalysts. The similar trends observed on model surfaces and supported catalysts demonstrate the feasibility of using single crystal surfaces to identify precious-metal-free bimetallic catalysts for biomass conversion.

1. Introduction

Biomass-derived molecules are a promising class of alternative energy resources to produce fuels and chemicals [1]. These molecules generally contain more oxygen atoms than are found in petroleum-based feedstocks, and the nature of oxygen over-functionalization plays a major barrier for the efficient utilization of biomass [2]. Controlling the activity and selectivity of the hydrodeoxygenation (HDO) reaction is critical for the upgrading of biomass feedstocks. Furfural [3], produced by the hydrolysis and dehydration of xylose from hemicellulose, is studied in this work as a model compound of biomass-derivatives containing carbon–oxygen bonds both within and outside the furan ring. One desirable reaction pathway of furfural is to produce an important biofuel, 2-methylfuran, through the HDO reaction.

It is critical to design a highly selective HDO catalyst for furfural reaction to produce 2-methylfuran. The HDO catalysts currently used are typically precious metals, such as Ru [4,5], Rh [6,7], Pd [6,8–10], Re [11] and Pt [6,12]. These catalysts exhibit relatively high activities, but also come with two significant drawbacks: (1) these catalysts often show side reactions involving C—C bond scission, leading to a reduction in the carbon chain length [10,11]; (2) these metals are limited in abundance and very expensive, which brings potential concerns for the large-scale production of cost-effective biomass-based fuels and chemicals [13]. Bimetallic catalysts are known to exhibit unique properties different from the parental metals [14,15]. Recently Sitthisa and Resasco have studied the reactions of furfural over SiO_2-supported Ni monometallic [16] and FeNi bimetallic [17] catalysts, with FeNi/SiO_2 being identified as a selective HDO catalyst for the conversion of furfural to the desired HDO product of 2-methylfuran. The work by Resasco et al. [17] has shown that the conversion of furfural on Ni/SiO_2 yielded primarily decarbonylation products, such as furan and CO. In comparison, on the FeNi/SiO_2 bimetallic catalyst, 2-methylfuran was found as the main product from the reaction of furfural with the decarbonylation products and their derivatives being suppressed.

Currently there is limited fundamental understanding of how the formation of the Fe—Ni bimetallic bonds affects the HDO pathway of furfural to produce 2-methylfuran. Our aim in this work is using monometallic Ni(1 1 1) and bimetallic Fe/Ni(1 1 1) surfaces in ultrahigh vacuum (UHV) environment to perform fundamental studies of the effect of bimetallic formation on the adsorption geometry and reaction pathways of furfural. Parallel DFT calculations also provide additional insight into the different bonding

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configurations of furfural over Ni(1 1 1) and Fe/Ni(1 1 1) surfaces. Finally, the adsorption geometry of furfural was investigated over Ni/SiO_2 and $FeNi/SiO_2$ catalysts under ambient pressure to bridge the materials gap and pressure gap between model surfaces and supported catalysts.

2. Theoretical and experimental methods

2.1. DFT calculations

All DFT calculations were performed with the Vienna *Ab initio* Simulation Package (VASP) [18–21]. The PW 91 functional [22] was used in the generalized gradient approximation (GGA) [23] calculation and a kinetic cutoff energy of 396 eV was chosen for the plane wave truncation. All slab calculations were performed using a periodic 4 × 4 unit cell with a 3 × 3 × 1 Monkhorst–Pack *k*-point grid. The clean Ni(1 1 1) surface was modeled by adding six equivalent layers of vacuum onto four Ni layers. The two bottom layers of the Ni(1 1 1) slab were frozen at a metal distance of 2.49 Å, while the top two layers were allowed to relax to reach the lowest energy configuration. The monolayer (ML) FeNi(1 1 1) surface was constructed by replacing the top layer of Ni atoms with Fe atoms. The FeNi alloy surface was modeled by replacing half of the Ni atoms in the top two layers with Fe atoms, with each Ni atom in the top two layers surrounded by a Fe atom, as shown in Fig. 1. The binding energy of furfural on each surface was calculated by subtracting the energies of the bare slab and free molecule from the total energy of the slab with adsorbed furfural.

2.2. Surface science experiments

Furfural (Sigma Aldrich, 99%), furfuryl alcohol (Sigma Aldrich, 98%) and 2-methylfuran (Sigma Aldrich, 99%) were transferred into separate glass sample cylinders and purified using freeze–pump–thaw cycles. All other gases, hydrogen, neon, carbon monoxide and propylene, were of research purity and used without further purification. The reagents were dosed into the UHV system through a stainless steel dosing tube and the purity was verified before experiments using mass spectrometry.

The temperature programmed desorption (TPD) measurements were performed in a UHV chamber with a base pressure of 1×10^{-10} Torr, equipped with Auger electron spectroscopy (AES), a mass spectrometer, a sputter gun and the Fe metal source, as described previously [24]. A Ni(1 1 1) single crystal (Princeton Scientific, 99.99%, 2 mm thick and 10 mm in diameter) was placed at the center of the UHV chamber by directly spot-welding to two tantalum posts, allowing resistive heating and cooling with liquid nitrogen. A chromel–alumel K type thermocouple was welded to the back of the Ni(1 1 1) sample for temperature measurement. The Ni(1 1 1) surface was cleaned using sputtering-annealing cycles. The ML FeNi(1 1 1) bimetallic surface was prepared by depositing Fe with the Ni(1 1 1) surface temperature held at 300 K. The FeNi alloy surface was prepared by depositing Fe with the Ni(1 1 1) surface at 650 K. The bimetallic surface composition was characterized using AES, as described previously [25]. The surface adsorbates and intermediates were identified using a high resolution electron energy loss spectroscopy (HREELS) housed in a separate UHV chamber equipped with AES, Fe source, sputter gun and HREELS, as described previously [26]. Each molecule was dosed to the surface at 100 K. Following the initial scan, the surface was flashed to the indicated higher temperatures at 3 K/s and cooled down to 100 K before each HREEL spectrum was recorded.

2.3. Synthesis of supported catalysts

The catalysts were prepared by incipient wetness co-impregnation of the support (Silica gel, from Sigma–Aldrich, Fluka 60741-1KG, BET surface area was 537 m^2/g) with an aqueous solution of the respective metal precursors ($Fe(NO_3)_2 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ from Alfa Aesar). The metal loading for each catalyst was listed in Table 1. After impregnation and drying in air at room temperature overnight, the samples were further dried and calcined in air with the following heating sequence: the temperature was increased to 373 K at a 0.4 K/min ramp and held at 373 K for 10 h, then increased to 773 K at a 1.0 K/min ramp and held at 773 K for 4 h.

2.4. Transmission electron microscopy (TEM)

TEM analysis was performed for Ni/SiO_2 and $FeNi/SiO_2$ catalysts using a JEOL2010F equipped with a Schottky field emission gun operated at 200 keV. Imaging was performed in the scanning transmission electron microscopy (STEM) mode with a 12 nm camera length and a 1.0 nm diameter, high-resolution nanoprobe. TEM samples were prepared by finely grinding reduced catalyst samples, and suspending the catalyst in ethanol. Droplets of the ethanol suspension were placed onto a carbon coated copper grid. The grids were allowed to fully dry before loading the samples into the TEM.

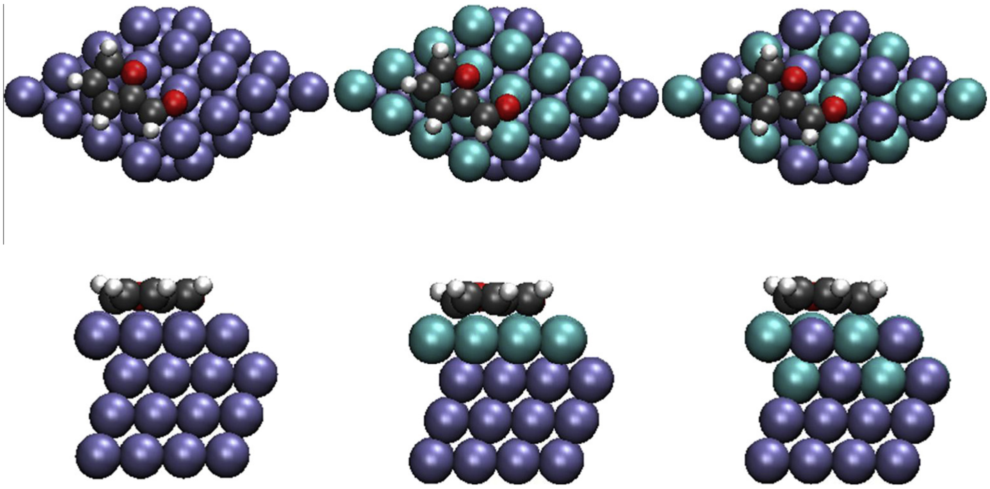

Fig. 1. Top and side views of the optimized configurations of furfural on Ni(1 1 1), ML FeNi(1 1 1) and FeNi alloy surfaces (Ni: iceblue, Fe: aqua, C: gray, O: red, H: white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)