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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(111) 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 SiO₂-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.

Keywords:

Fe/Ni(111) surfaces; FeNi/SiO₂ catalysts; furfural; 2-methylfuran; furfuryl alcohol; hydrodeoxygenation (HDO); bimetallic effects

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 Resasco and the co-workers have studied the reactions of furfural over SiO₂-supported Ni monometallic [16] and FeNi bimetallic [17] catalysts, with FeNi/SiO₂ 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/SiO₂ yielded primarily decarbonylation products, such as furan and CO. In comparison, on

the FeNi/SiO₂ 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(111) and bimetallic Fe/Ni(111) 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 configurations of furfural over Ni(111) and Fe/Ni(111) surfaces. Finally, the adsorption geometry of furfural was investigated over Ni/SiO₂ and FeNi/SiO₂ 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 $3 \times 3 \times 1$ Monkhorst-Pack k-point grid. The clean Ni(111) surface was modeled by adding six equivalent layers of vacuum onto four Ni layers. The two bottom layers of the Ni(111) 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(111) 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 Figure 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(111) 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(111) sample for temperature measurement. The Ni(111) surface was cleaned using sputtering-annealing cycles. The ML FeNi(111) bimetallic surface was prepared by depositing Fe with the Ni(111) surface temperature held at 300 K. The FeNi alloy surface was prepared by depositing Fe with the Ni(111) 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 m²/g) with an aqueous solution of the respective metal precursors (Fe(NO₃)₂•9H₂O, Ni(NO₃)₂•6H₂O from Alfa Aesar). The metal loading for each catalyst was listed in the 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 hours, then increased to 773 K at a 1.0 K/min ramp and held at 773 K for 4 hours.

2.4 Transmission Electron Microscopy (TEM)

TEM analysis was performed for Ni/SiO₂ and FeNi/SiO₂ 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.

2.5. Extended X-ray Absorption Fine Structure (EXAFS)

Ni K-edge EXAFS measurements were collected in order to detect and characterize the formation of Fe–Ni bimetallic bonds. The measurements were performed on the X18A Beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The FeNi/SiO₂ catalyst was pre-reduced at 773 K under a constant flow of hydrogen and helium for 1.5 hours before the EXAFS experiments. After pre-reduction, a catalyst pellet was prepared for the EXAFS experiment. The procedures for the sample preparation and data collection have been previously reported [27]. Before performing EXAFS measurements at room temperature, the FeNi/SiO₂ pellet was re-reduced in a constant flow of hydrogen and helium at 723 K.

The EXAFS results were analyzed using the IFFEFIT 1.2.11 data analysis package (Athena, Artemis, Atoms, and FEFF6) [28-30], as described in detail previously [27]. In fitting the data for the FeNi/SiO₂ catalyst, both the Ni–Ni and Ni–Fe contributions to the theoretical EXAFS were taken into account. The Ni–Fe contributions were modeled by replacing Ni with Fe in the first nearest neighbor shell. The passive electron reduction factor was found to be 0.82 from the fitting of Ni foil data, and this value was fixed for the fitting of the FeNi/SiO₂ catalyst.

2.6. Fourier Transform Infrared (FTIR) Spectroscopy of Supported Catalysts

The FTIR was used to record vibrational spectra of furfural adsorbed on the Ni/SiO₂ and FeNi/SiO₂ catalysts after 3 reduction cycles in 30 Torr of hydrogen at 773 K for 30 minutes. The design of the IR cell has been reported elsewhere [27]. The FTIR spectra of adsorbed furfural were recorded with 4 cm⁻¹ resolution using a Thermo Nicolet Nexus 470 spectrometer equipped with a MCT-A (mercury cadmium telluride) detector.

3. Results

3.1. DFT Calculations of Furfural on Fe/Ni(111) Surfaces

DFT calculations of furfural were performed on Ni(111), ML FeNi(111) and FeNi alloy surfaces. The top and side views of the optimized configurations of furfural on these three surfaces are shown in Figure 1. Furfural is adsorbed on the three surfaces in through both the furan ring and carbonyl group. For FeNi alloy surface, the Fe and Ni atoms remain a 1:1 ratio in the top two layers, with each Ni atom in the top two layers surrounded by a Fe atom. Both Fe and Ni atoms are directly involved in bonding to furfural. For example, as shown in Figure 1, the carbon and oxygen atoms in the carbonyl group in furfural are bonded to the Ni and Fe atoms, respectively. Table 2 summarizes the DFT calculation results of furfural binding energies on the three surfaces as well as the corresponding bond lengths. The assignment of the carbon and oxygen atoms in furfural is shown in Figure 2. Different from gas phase furfural species, upon adsorption the C-C bond lengths in furfural increase, indicating a slight enlargement of the ring resulting from the interaction with the surface. An increase is also observed in the C1-O1 bond distance due to the interaction between the carbonyl group and the surfaces. The increase of bond lengths in both the furan ring and carbonyl group agrees with the optimized furfural adsorption configuration on the three surfaces shown in Figure 1.

As shown in Table 2, compared with Ni(111), ML FeNi(111) shows a higher furfural binding energy (-31.61 kcal/mol). Furthermore, the C1-O1 bond length of furfural is larger on ML FeNi(111) than that on Ni(111), indicating that the addition of Fe makes the surface to bind with the carbonyl group of furfural more strongly. Table 2 also compares the bond distances between furfural atoms with surface metal atoms on the three surfaces. Compared with Ni(111), the addition of ML Fe results in a reduction in the O1-M bond distance and an increase in the C1-M bond length, indicating the carbonyl group in furfural on ML FeNi(111) surface is more

tilted. In addition, the bond lengths of C3-M, C5-M and O2-M are significantly longer on ML FeNi(111) surface than on Ni(111), indicating that the furan ring is more tilted on the ML FeNi(111) surface.

3.2. TPD Experiments of Furfural on Fe/Ni(111) Surfaces

TPD experiments of furfural were performed on the Ni(111), ML FeNi(111), FeNi alloy and thick Fe surfaces. Figure 3 displays the TPD spectra of the products from furfural reactions on the four surfaces. As shown in Figure 3a, hydrogen desorbs from the Ni(111), ML FeNi(111), FeNi alloy and thick Fe surfaces at 390 K, 415 K, 385 K and 390 K, respectively. In Figure 3b, the decomposition of furfural leads to the desorption of CO at 415 K from Ni (111), 380 K from ML FeNi(111), 385 K from FeNi alloy and 365 K from thick Fe. Figure 3c shows the desorption of propylene from the reaction of furfural. The desorption of the propylene product is found to occur at 270 K and 315 K on Ni(111), at 315 K on FeNi alloy and at 320 K on thick Fe. The production of propylene on the ML FeNi(111) surface is negligible. Figure 3d compares the desorption of 2-methylfuran from the four surfaces. The 2-methylfuran product is not observed on the Ni(111) surface. The desorption of 2-methylfuran is found at 325 K, 300 K and 320 K from ML FeNi(111), FeNi alloy and thick Fe surfaces, respectively.

3.3. TPD Experiments of Furfural on Hydrogen Pre-dosed Fe/Ni(111) Surfaces

In order to study the effect of pre-dosed hydrogen, the TPD experiments of furfural were carried out on the hydrogen pre-dosed Fe/Ni(111) surfaces, as shown in Figure 4. Furfuryl alcohol is not observed on the four surfaces. It is possible that once furfuryl alcohol is formed on the surface, it would quickly react to form other products, for example, 2-methylfuran and propylene. In order to confirm this hypothesis, TPD experiments of furfuryl alcohol on Fe/Ni(111) surfaces were performed and the results were shown in the next section. In Figure

4b, the desorption peaks of CO from furfural decomposition are observed at 420 K on H/Ni(111), 390 K on H/ML FeNi(111), 390 K on H/FeNi alloy and 360 K on H/thick Fe surfaces. Figure 4c is the desorption profile of propylene from the reaction of furfural, with propylene desorbing between 270 K and 320 K from the four surfaces. Figure 4d compares the desorption of 2-methylfuran. The production of 2-methylfuran is found at 335 K, 300 K and 315 K from ML FeNi(111), FeNi alloy and thick Fe surfaces, respectively.

One should notice that on hydrogen pre-dosed surface, the desorption peak areas of propylene and 2-methylfuran increase significantly, indicating pre-dosed hydrogen is necessary for the production of propylene and 2-methylfuran from furfural. This is consistent with the hydrogen balance in Reactions (1) and (2) shown below.

As shown in Figure 3 and Figure 4, hydrogen, CO, propylene and 2-methylfuran are observed as the reaction products of furfural from the Fe/Ni(111) surfaces, and the corresponding net reaction pathways of furfural on the four surfaces can be summarized as below:

Reaction (1) is the desirable 2-methylfuran production pathway, which involves a HDO reaction through the C=O functional group to produce 2-methylfuran and O_{ad}. Reaction (2) is the propylene production pathway that involves the cleavages of C1-C2, C2-C3 and C5-O2 bonds of furfural to produce propylene and CO. Reaction (3) is the reforming pathway involving the C-C

bond scission with the C-O/C=O bonds remaining intact to produce syngas. Reaction (4) represents the total decomposition pathway, producing H₂, as well as C_{ad} and O_{ad}. The values of a, b, c and d, represent the amount of furfural undergoes each reaction pathway, and can be calculated as follows:

$$\text{2-methylfuran yield} = a \rightarrow a = \text{2-methylfuran yield}$$

$$\text{propylene yield} = b \rightarrow b = \text{propylene yield}$$

$$\text{CO yield} = 2b + 2c \rightarrow c = 0.5 * \text{CO yield} - b$$

$$\text{H}_2 \text{ yield} = 2c + 2d \rightarrow d = 0.5 * \text{H}_2 \text{ yield} - c$$

In order to quantify the amount of furfural following each reaction pathway, the yields of H₂ and CO products were obtained by comparing their TPD peak areas with those after saturation exposures of H₂ and CO on Ni(111). In the quantification, the literature saturation coverages of H₂ (1 ML [31]) and CO (0.5 ML [32]) on Ni(111) were used. The yields of propylene and 2-methylfuran were determined using experimentally determined sensitivity factors relative to CO, which were obtained by back filling the UHV system with equal concentrations of propylene and 2-methylfuran relative to CO based on the ionization sensitivity factors. The details about the quantification method was similar to that described previously for other molecules [33].

The quantification results of furfural reaction on the H/Ni(111), H/ML FeNi(111), H/FeNi alloy and H/thick Fe surfaces are summarized in Table 3. Since there is hydrogen pre-dosed on the four surfaces, which would affect the hydrogen balance, the amount of furfural undergoing the total decomposition pathway is not listed in Table 3. According to the quantification results, the H/Ni(111) surface shows the highest reforming and total activity for furfural reaction. On the H/Ni(111) surface, the activity of 2-methylfuran production pathway is

zero. However, when the surface is modified with Fe, furfural reacts and produces the desired 2-methylfuran. Among all the four surfaces, the H/ML FeNi(111) shows the highest activity for the 2-methylfuran production pathway.

3.4. TPD Experiments of Furfuryl Alcohol on Fe/Ni(111) Surfaces

In order to verify the reaction mechanism hypothesis that the production of 2-methylfuran from furfural involves a hydrogenation and the subsequent hydrogenolysis in the carbonyl group, in which process furfuryl alcohol is produced as an intermediate, TPD experiments of furfuryl alcohol were performed on the Fe/Ni(111) surfaces. Figure 5a shows the TPD spectra of 2-methylfuran production with the exposure of furfural alcohol on Ni(111), ML FeNi(111), FeNi alloy and thick Fe/Ni(111) surfaces. On the clean Ni(111) surface, a desorption peak of 2-methylfuran is observed at 295 K. The desorption peaks of 2-methylfuran are observed on the ML FeNi(111), FeNi alloy and thick Fe surfaces at 325 K, 300 K and 310 K, respectively, similar with those in the TPD spectra following the production of 2-methylfuran from furfural.

As shown in Figure 4 and Figure 5a, both furfural and furfuryl alcohol react on hydrogen pre-dosed Fe-modified Ni(111) surfaces to produce 2-methylfuran, on which H/ML FeNi(111) shows the highest activity. Figure 5b compares the desorption peaks of 2-methylfuran on H/ML FeNi(111) surface with the exposure of 4L furfuryl alcohol and 4L furfural. The desorption temperature of 2-methylfuran is similar from the two molecules, indicating that furfuryl alcohol is a likely intermediate in furfural reaction to produce 2-methylfuran. Furthermore, the peak area of 2-methylfuran from furfuryl alcohol is much larger than that from furfural, suggesting that the hydrogenation step of furfural is critical for the formation of 2-methylfuran.

Propylene is also observed as a product from furfural reaction on H/Ni(111), H/ML FeNi(111), H/FeNi alloy and H/thick Fe surfaces. On the ML FeNi(111) surface without pre-

dosed hydrogen, the peak area of propylene is negligible, likely due to the fact that extra hydrogen is needed for the production of propylene based on the hydrogen balance. This is consistent with the presence of a propylene desorption peak with pre-dosed hydrogen on the surface. In the TPD experiments of furfuryl alcohol on Fe/Ni(111) surfaces, no propylene is observed as the product, indicating that furfuryl alcohol is not the intermediate of propylene production from furfural.

3.5. HREELS of Furfural on Hydrogen Pre-dosed Fe/Ni(111) Surfaces

HREELS experiments were performed to identify the surface reaction intermediates and their binding configurations on the surfaces. Figure 6 shows the HREEL spectra of 4L furfural on H/Ni(111), H/ML FeNi(111) and H/FeNi alloy surfaces. The vibrational modes of furfural are summarized in Table 4. At 100 K the HREEL spectra of adsorbed furfural (Figure 6a) on all three surfaces generally match with the Raman spectrum of liquid-phase furfural, indicating that furfural is molecularly adsorbed on the three surfaces. The vibrational peaks at 602 cm^{-1} , 1637 cm^{-1} and 3112 cm^{-1} represent the $\tau(\text{ring})$, $\nu(\text{C=O})$ and $\nu(\text{CH})$ modes, respectively. The peak at around 3396 cm^{-1} can be assigned to the adsorbed water from the background of the UHV chamber.

In Figure 6b, when the surfaces are heated to 200 K, the HREELS spectra on all three surfaces change significantly. The relative intensities of the peak assigned to the C-H bond of the furan ring at 3071 cm^{-1} decrease compared to those of the aliphatic C-H bond at 2882 cm^{-1} , indicating the enhanced interaction between the furan ring and the metal surfaces. The intensities of the $\nu(\text{C=O})$ mode decrease as well, suggesting a strong interaction between the C=O bond and the surfaces. These combined observations indicate that furfural is adsorbed on the surfaces

through both the furan ring and the carbonyl group, consistent with the optimized adsorption configuration from the DFT calculations.

In order to understand the effect of bimetallic formation on the adsorption geometry and reaction pathways of furfural, off-specular HREELS measurements were performed to determine the difference between the binding configurations of furfural on Ni(111) and ML FeNi(111) surfaces. The off-specular HREELS measurements often provide information regarding the orientation of the adsorbates. The surface dipole selection rule dictates that vibrational motions with dipole moments parallel to a metal surface would not be observed. In the specular HREELS measurements, where the incident and scattering angles of the electron beam are the same, the intensities of vibrational modes are contributed mainly from dipole scattering. On the other hand, for off-specular measurements, where the incident and scattering angles of the electron beam are no longer the same, the non-dipole scattering event contributes more to the intensities. For example, for a vibrational mode that is parallel to a metal surface, its relative intensity would increase from specular to off-specular HREELS measurements.

Figure 7 compares the on- and off-specular HREEL spectra of 0.5 L furfural at 100 K on Ni(111) and ML FeNi(111) surfaces. As summarized in Table 4, vibrational peaks at 1423 cm^{-1} and 1618 cm^{-1} represent the $\nu(\text{C}=\text{C})$ mode in the furan ring and the $\nu(\text{C}=\text{O})$ mode in the carbonyl group, respectively. The ratio of these two peaks, $I(1423)/I(1618)$, is summarized in Table 5 for the on- and off-specular measurements. The change in the value of $I(1423)/I(1618)$ from on-specular to off-specular HREELS provides a qualitative information regarding the relative orientation of the furan ring in furfural with respect to the carbonyl group. Here Θ is defined as the tilted degree of the furan ring or carbonyl group to the surface. As shown in Table 5, $I(1423)/I(1618)$ on Ni(111) changes from 2.4 to 3.4, increasing more than 40%, suggesting that

the furan ring in furfural is adsorbed more parallel to the Ni(111) surface than the carbonyl group ($\Theta_{\text{ring/Ni}} < \Theta_{\text{C=O/Ni}}$). In contrast, on the ML FeNi(111) surface, the I(1423)/I(1618) ratio remains similar between the on- and off-specular HREELS, indicating that the furan ring in furfural is tilted in a similar angle as the carbonyl group to ML FeNi(111) surface ($\Theta_{\text{ring/ML FeNi}} = \Theta_{\text{C=O/ML FeNi}}$). As shown in the DFT calculation results, the carbonyl group is more tilted on ML FeNi(111) surface than on Ni(111) ($\Theta_{\text{C=O/Ni}} < \Theta_{\text{C=O/ML FeNi}}$). Similarly, the on- and off-specular HREELS results reveal a relationship of $\Theta_{\text{ring/Ni}} < \Theta_{\text{ring/ML FeNi}}$ and indicate that the furan ring is more tilted on the ML FeNi(111) surface than on Ni(111). Nearly identical on- and off-specular dependence was obtained for furfural adsorbed on Ni(111) and ML Fe/Ni(111) with pre-adsorbed hydrogen (spectra not shown), indicating that the orientation of furfural is not affected by the presence of atomic hydrogen on the surfaces.

3.6. TEM and EXAFS Results of Supported Catalysts

TEM imaging was performed to characterize the particle size of the reduced Ni/SiO₂ and FeNi/SiO₂ catalysts. Figure 8 shows the high-angle annular dark field (HAADF) TEM images and particle size distributions of the catalysts. The dominant population in each catalyst appears to be relatively uniform. As summarized in Table 1, the average particle sizes were found to be 5.7 nm and 2.4 nm for the Ni/SiO₂ and FeNi/SiO₂ catalysts, respectively.

Figure 9a and 9b show the Ni and Fe K-edge X-ray absorption near-edge structure (XANES) spectra for the FeNi/SiO₂ catalyst before and after reduction, along with the Ni and Fe foil spectra for reference. The Ni and Fe K-edge XANES reveal information regarding the extent of oxidation of the FeNi/SiO₂ sample. Relatively intense peaks at 8350 eV in Figure 9a and 7130 eV in Figure 9b before reduction are attributed to the formation of the Ni-O and Fe-O bonds in the FeNi/SiO₂ catalyst, respectively. After H₂ treatment, the white-line features disappear and the

intensities approach those of Ni and Fe foils. The changes in the spectra in Figure 9a and 9b indicate that Ni and Fe are in the metallic state after H₂ reduction.

Figure 9c shows Fourier transformed (magnitude) k^2 -weighted Ni K-edge EXAFS function ($\chi(k)$) along with the fit obtained using FEFF6 theory. Since Fe K-edge energy (7112eV) is closely followed by that of Ni (8333eV), the EXAFS scans might be affected by Ni K-edge contributions, and therefore the Fe K-edge EXAFS figure is not shown here. The EXAFS data were analyzed by only including the Ni-Ni and Ni-Fe contributions; the Ni-O and Fe-O contributions were neglected in the fitting based on the XANES spectra of the reduced FeNi/SiO₂ sample. For bulk metals, the Ni-Ni distance is 2.49 Å and the Fe-Fe distance is 2.58 Å for fcc structure and 2.54 Å for bcc structure. According to the fit of the Fourier transformed spectra in Figure 9c, the Ni-Fe distance in FeNi/SiO₂ ranges from 2.55 Å to 2.57 Å, which is an intermediate value between the two monometallic distances, further suggesting the formation of Fe-Ni bimetallic bonds in the FeNi/SiO₂ catalyst.

3.7. FTIR Spectra of Furfural Adsorption on Supported Catalysts

After the reduction of catalysts in H₂ at 773 K, furfural vapor was introduced into the batch reactor. The FTIR spectra of furfural on the Ni/SiO₂ and FeNi/SiO₂ catalysts at 300 K and 373 K are shown in Figure 10. The intensity ratios of $\nu(\text{C}=\text{C})$ (1470cm⁻¹)/ $\nu(\text{C}=\text{O})$ (1670cm⁻¹) in the FTIR spectra of adsorbed furfural on Ni/SiO₂ and FeNi/SiO₂ are summarized in Table 6.

As shown in Figure 10, on the Ni/SiO₂ catalyst the $\nu(\text{C}=\text{C})$ peak intensity is lower than that of the $\nu(\text{C}=\text{O})$ peak with a ratio of $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{O})$ around 0.68 at 300 K and 0.64 at 373 K. In comparison, on the FeNi/SiO₂ catalyst the $\nu(\text{C}=\text{C})$ peak is more intense than the $\nu(\text{C}=\text{O})$ peak with a ratio of $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{O})$ around 1.33 at 300 K and 1.30 at 373 K. These combined observations indicate that the furan ring interacts more strongly with Ni/SiO₂ than with

FeNi/SiO₂, consistent with the DFT and off-specular HREELS results on the corresponding single crystal surfaces.

4. Discussion

4.1. Effect of Fe Addition onto Ni(111) Surface for Furfural Reaction

Based on DFT calculations and off-specular HREELS results, furfural is adsorbed on the Ni(111) surface through both the furan ring and the carbonyl group with the furan ring more parallel to the surface. In the reaction of furfural on the Ni(111) and H/Ni(111) surfaces, furan or C₄ molecules (such as 1,3-butadiene, 1-butene or butane) are not observed as a reaction product, suggesting a dissociation of the furan ring in the reaction of furfural with both C-C and C-O bond scission. This is consistent with the DFT calculation results that the furan ring interacts more strongly with the Ni(111) surface through the more parallel binding configuration of the furan ring.

When Ni(111) surface is modified with Fe, the desired reaction product, 2-methylfuran is observed. Based on the HREELS results, furfural is adsorbed primarily through the carbonyl group with the furan group further tilted away from the ML Ni/Fe(111) surface. The DFT results also reveal that, with the addition of Fe on Ni(111), the C1-O1 bond length of furfural is longer than that on Ni(111), indicating that furfural is bonded onto the ML FeNi(111) surface more strongly through the carbonyl group. Furthermore, compared with the Ni(111) surface, the addition of Fe reduces the O1-M bond distance and increases the C1-M bond length. The enhancement of the binding through the carbonyl group and the change in the O1-M and C1-M bond lengths might be responsible for the furan ring to be further tilted away from the surface, advantageous for the HDO reaction through the carbonyl group to produce the desirable 2-methylfuran. This adsorption configuration is also consistent with the TPD results that, compared

with the Ni(111) surface, the reforming activity of furfural involving C-C bond cleavage is suppressed on the ML FeNi(111) surface.

4.2. Correlating Model Fe/Ni(111) Surfaces with Supported Fe/Ni Catalysts

The bonding configurations derived from the Ni(111) and ML FeNi(111) surfaces are consistent with the results observed in the FTIR spectra of adsorbed furfural on the SiO₂-supported Ni and FeNi catalysts. As shown Figure 10 and summarized in Table 6, the $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{O})$ peak ratio is lower on Ni/SiO₂ than on FeNi/SiO₂, consistent with the furan ring interacting more strongly with the monometallic Ni catalyst than the FeNi bimetallic catalyst. The agreement of furfural adsorption configuration on the ML FeNi(111) surface and SiO₂-supported FeNi catalyst helps to understand the correlation between the formation of Fe-Ni bimetallic bonds and the adsorption configuration of furfural on catalytic surfaces. The similarity in adsorption geometry leads to the consistency in the HDO of furfural on model Fe/Ni(111) surfaces and previous results on supported Fe/Ni catalysts [17]. Furfural reacts on the ML FeNi(111) surface to produce the desirable reaction product of 2-methylfural, which is not observed on the clean Ni(111) surface due to the dissociation of the furan ring in furfural into smaller products. The results are consistent with the work by Resasco et al. [17] that 2-methylfuran is found as the main product from furfural reaction on FeNi/SiO₂ catalysts.

5. Conclusions

In this work, the adsorption geometry and reaction pathways of furfural on precious-metal-free Fe/Ni(111) surfaces are investigated using DFT calculations and surface science experiments. On the ML FeNi(111) bimetallic surface, 2-methylfuran, an important biofuel, is observed as a reaction product from furfural through the selective HDO reaction via the carbonyl

group. The results from surface science study on model Fe/Ni(111) surfaces together with the FTIR spectra on SiO₂-supported Fe/Ni catalysts as well as the work by Resasco et al. reveal the effect of Fe-Ni bimetallic bond formation on the adsorption geometry and the reaction pathways of furfural. The consistency between Fe/Ni(111) model surfaces and supported Fe/Ni catalysts shows the feasibility of using single crystal surfaces to identify precious-metal-free bimetallic catalysts for HDO and potentially other types of catalytic reactions.

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Figure and Table Captions

Figure 1. Top and side views of the optimized configurations of furfural on Ni(111), ML FeNi(111) and FeNi alloy surfaces (Ni: iceblue, Fe: aqua, C: grey, O: red, H: white).

Figure 2. Assignment of atoms in furfural.

Figure 3. TPD spectra of (a) hydrogen ($m/e=2$), (b) CO ($m/e=28$), (c) propylene ($m/e=41$) and (d) 2-methylfuran ($m/e=53$) with an exposure of 4L furfural on Ni(111) and Fe/Ni(111) surfaces.

Figure 4. TPD spectra of (a) furfuryl alcohol ($m/e=98$), (b) CO ($m/e=28$), (c) propylene ($m/e=41$) and (d) 2-methylfuran ($m/e=53$) with an exposure of 4L furfural on hydrogen pre-dosed Ni(111) and Fe/Ni(111) surfaces.

Figure 5. (a) TPD spectra of 2-methylfuran ($m/e=53$) with an exposure of 4L furfuryl alcohol on Ni(111) and Fe/Ni(111) surfaces. (b) Comparison of TPD spectra of 2-methylfuran ($m/e=53$) with an exposure of 4L furfuryl alcohol and 4L furfural on hydrogen pre-dosed ML FeNi(111) surfaces.

Figure 6. HREELS of 4 L furfural on H/Ni(111), H/ML FeNi(111) and H/FeNi alloy surfaces at (a) 100 K and (b) 200 K.

Figure 7. On and off-specular HREELS of 0.5 L furfural on Ni(111) and ML FeNi(111) surfaces at 100 K.

Figure 8. HAADF TEM micrographs and particle size distribution for (a) Ni/SiO₂ and (b) FeNi/SiO₂.

Figure 9. (a) Ni and (b) Fe K-edge XANES spectra before and after reduction. The Ni and Fe foils are included to serve as a reference. (c) Fourier transformed (magnitude) k^2 -weighted EXAFS function ($\chi(k)$) of Ni K-edge after reduction.

Figure 10. FTIR spectra of furfural adsorption on Ni/SiO₂ and FeNi/SiO₂ catalysts.

Table 1. Catalysts compositions and particle size distribution from TEM measurements

Table 2. Comparison of bond lengths (Å) and binding energies (kcal/mol) of furfural in gas phase and adsorbed on the corresponding surfaces

Table 3. Reaction activity of furfural on hydrogen pre-dosed Fe/Ni(111) surfaces from TPD measurements

Table 4. Vibrational mode assignment of furfural

Table 5. Intensity ratio of $\nu(\text{C}=\text{C})$ (1423 cm⁻¹)/ $\nu(\text{C}=\text{O})$ (1618 cm⁻¹) in HREEL spectra of furfural adsorption on Ni(111) and ML FeNi(111) surfaces

Table 6. Intensity ratio of $\nu(\text{C}=\text{C})$ (1470 cm⁻¹)/ $\nu(\text{C}=\text{O})$ (1670 cm⁻¹) in FTIR spectra of furfural adsorption on Ni/SiO₂ and FeNi/SiO₂ catalysts

Figure 1. Top and side views of the optimized configurations of furfural on Ni(111), ML FeNi(111) and FeNi alloy surfaces (Ni: iceblue, Fe: aqua, C: grey, O: red, H: white).

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Figure 7. On and off-specular HREELS of 0.5 L furfural on Ni(111) and ML FeNi(111) surfaces at 100 K.

Figure 8. HAADF TEM micrographs and particle size distribution for (a) Ni/SiO₂ and (b) FeNi/SiO₂.

	CN(Ni-Ni)	CN(Ni-Fe)	d(Ni-Ni)	d(Ni-Fe)	ss(Ni-Ni)	ss(Ni-Fe)
FeNi/SiO ₂	3.66 ± 0.53	3.61 ± 0.42	2.44 ± 0.01	2.56 ± 0.01	0.002 ± 0.001	0.002 ± 0.001

Figure 9. (a) Ni and (b) Fe K-edge XANES spectra before and after reduction. The Ni and Fe foils are included to serve as a reference. (c) Fourier transformed (magnitude) k^2 -weighted EXAFS function ($\chi(k)$) of Ni K-edge after reduction.

Figure 10. FTIR spectra of furfural adsorption on Ni/SiO_2 and FeNi/SiO_2 catalysts.

Table 1. Catalysts compositions and particle size distribution from TEM measurements

Catalyst	Metal loading (wt %)	Molar ratio (Fe:Ni)	Average diameter (nm)
Ni/SiO ₂	1.4	---	5.7 ± 0.8
FeNi/SiO ₂	1.3 : 1.4	1:1	2.4 ± 0.4

Table 2. Comparison of bond lengths ($\text{\AA}$) and binding energies (kcal/mol) of furfural in gas phase and adsorbed on the corresponding surfaces

	Gas phase	Ni(111)	ML FeNi(111)	FeNi alloy
C1-H1	1.120	1.099	1.094	1.095
C1-O1	1.229	1.320	1.340	1.349
C1-C2	1.448	1.435	1.422	1.430
C2-C3	1.382	1.433	1.430	1.435
C3-C4	1.419	1.425	1.440	1.411
C4-C5	1.373	1.449	1.449	1.446
C5-O2	1.359	1.474	1.471	1.466
O2-C2	1.378	1.409	1.414	1.401
O1-M	-	1.954	1.922	1.930
C1-M	-	2.099	2.291	2.097
C2-M	-	2.165	2.168	2.223
C3-M	-	2.085	2.392	2.281
C4-M	-	2.108	2.052	2.248
C5-M	-	1.995	2.207	2.125
O2-M	-	2.089	2.167	2.226
Binding Energy	-	-20.34	-31.61	-18.50

Table 3. Reaction activity of furfural on hydrogen pre-dosed Fe/Ni(111) surfaces from TPD measurements

Activity (monolayer per metal atom)				
	2-methylfuran production (a)	Propylene production (b)	Reforming (c)	Total activity
H/Ni(111)	0.000	0.003	0.108	0.111
H/ML FeNi(111)	0.012	0.002	0.075	0.089
H/FeNi alloy	0.003	0.008	0.081	0.092
H/thick Fe	0.007	0.002	0.056	0.065

Table 4. Vibrational mode assignment of furfural

Mode	Frequency (cm ⁻¹)	
	^a Raman	H/Ni(111) ^b
τ (ring)		602
ω (CH)		771
δ (ring)		
ν (CO)	930	
χ (CH)	950	
ν (CO)	1025	1021
δ_b (O-C-H)	1157	
ρ (CH)		
δ_b (O-C-H)	1370	
ν (CC)	1395	
ν (C=C)	1466, 1555, 1570	1448
ν (C=O)	1684	1637
ν (CH)		2882
ν (CH)	3153	3112
τ – torsion, ω - wagging, δ - deformation, χ – scissoring, δ_b – bending, ν –stretching		

^a Reference [34]

^b 4 L furfural on H/Ni(111) at 100 K

Table 5. Intensity ratio of $\nu(\text{C}=\text{C})$ (1423 cm^{-1})/ $\nu(\text{C}=\text{O})$ (1618 cm^{-1}) in HREEL spectra of furfural adsorption on Ni(111) and ML FeNi(111) surfaces

	Type	I(1423)/I(1618)
Ni(111)	On-specular	2.4
	Off-specular	3.4
ML FeNi(111)	On-specular	2.9
	Off-specular	3.0

Table 6. Intensity ratio of $\nu(\text{C}=\text{C})$ (1470 cm^{-1})/ $\nu(\text{C}=\text{O})$ (1670 cm^{-1}) in FTIR spectra of furfural adsorption on Ni/SiO₂ and FeNi/SiO₂ catalysts

	300 K	373 K
Ni/SiO ₂	0.68	0.64
FeNi/SiO ₂	1.33	1.30

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