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**Selective hydrogenation of biomass-derived 2(5H)-furanone over
Pt-Ni and Pt-Co bimetallic catalysts: From model surfaces to
supported catalysts**

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Abstract

The selective hydrogenation of biomass-derived 2(5H)-furanone to γ -butyrolactone (GBL) was studied over Pt-Ni and Pt-Co bimetallic model surfaces and supported catalysts. The reactions of 2(5H)-furanone were investigated on Ni/Pt(111) and Co/Pt(111) bimetallic surfaces using temperature-programmed desorption (TPD), revealing that the Ni-terminated bimetallic Ni-Pt-Pt(111) surface was more active and selective to produce GBL. Parallel density functional theory (DFT) calculations also confirmed the higher hydrogenation activity on Ni-Pt-Pt(111) due to bimetallic effect. The promising results on model surfaces were extended to SiO₂-supported catalysts. The hydrogenation activity in terms of the initial turnover frequency (TOF) followed the trend of Pt-Ni > Pt-Co > Pt > Ni > Co, where the TOF over Pt-Ni was almost twice higher than that over Pt. With the excellent correlation between model surfaces and supported catalysts, the Pt-Ni bimetallic catalyst was identified as a promising option for the selective hydrogenation of 2(5H)-furanone to GBL.

Keywords: 2(5H)-Furanone; γ -Butyrolactone; Selective hydrogenation; Ni/Pt(111) surfaces; Co/Pt(111) surfaces; Bimetallic catalysts

1. Introduction

Biomass-derived molecules can serve as a renewable source for the sustainable production of fuels and chemicals [1,2]. During the past decades, novel synthetic methods and catalytic processes have been developed for the synthesis of C₄ biomass-derived molecules such as succinic acid, maleic acid and 2(5H)-furanone [3-5]. For example, many efforts have focused on the production of 2(5H)-furanone by oxidation of furfural, which can be easily produced from lignocellulose [6], and a reasonable yield of 2(5H)-furanone over 60% was achieved in our recent work [7]. However, the potential for further conversion of 2(5H)-furanone to high value-added chemicals remains largely unexplored [8]. In view of the chemical structure, 2(5H)-furanone has only one more additional C=C bond than γ -butyrolactone (GBL). Thus it is a promising platform compound to produce GBL and 1,4-butanediol (BDO), which can be widely used as monomers, solvents and perfumes [9,10]. The selective hydrogenation of the C=C bond of 2(5H)-furanone allows the design of an optimum reaction pathway with high atom economy starting from a renewable oxygenate to the target product, GBL.

In our previous work, the selective hydrogenation of 2(5H)-furanone to GBL was studied over a series of SiO₂-supported Group VIII monometallic catalysts [11]. It showed that Pd and Rh exhibited better catalytic performances than other monometallic catalysts such as Pt, Ru, Ni, Co and Cu. However, further studies are needed to understand the descriptors that control the hydrogenation activity and selectivity. The Pt-based bimetallic catalysts have shown very different electronic and chemical properties compared with their parent metals [2,12-14]. Enhancing the activity and/or selectivity of the Pt catalysts by adding a second metal has been verified for the selective hydrogenation of C=C bond in many reactions. For example, Lu *et al.* [15] studied the

selective hydrogenation of cyclohexene over γ -Al₂O₃ supported Pt, Pt-Ni and Pt-Co catalysts, with the rate constants of 1.7, 27 and 21 min⁻¹ for Pt/ γ -Al₂O₃, Pt-Ni/ γ -Al₂O₃ and Pt-Co/ γ -Al₂O₃, respectively. Zheng *et al.* [16] reported the controlled hydrogenation of C=C and C=O bonds in cinnamaldehyde over SiO₂-supported Pt-Co and Pt-Cu bimetallic catalysts. The results indicated that both catalysts were more active than the monometallic catalysts, and that Pt-Co enhanced the hydrogenation of C=O bond while Pt-Cu preferred the hydrogenation of C=C bond. Li *et al.* [17] showed that for the hydrogenation of maleic anhydride, the addition of Ni to Pt increased both the hydrogenation activity and selectivity to succinic acid, and the Pt-Ni/Al₂O₃ bimetallic catalyst was more active and selective than Pd/Al₂O₃ and RhCl₂(TPP)₃ [18,19]. Overall, most of the Pt-based bimetallic catalysts reported in the literature exhibited improved hydrogenation activity and different selectivity compared with the corresponding monometallic catalysts. However, there have been no studies on the utilization of Pt-based bimetallic catalysts for 2(5H)-furanone hydrogenation.

As a highly functionalized C₄ molecule, 2(5H)-furanone has two unsaturated bonds, namely the C=C and C=O bonds, and it also contains two C-O bonds within the ring. As a result, different adsorption geometries and strengths of 2(5H)-furanone can exist on the catalyst surface, which may favor different reaction pathways, such as the selective hydrogenation of the C=C or C=O bond, and the ring opening *via* C-O bond scission. In the past decade, surface science experiments and density functional theory (DFT) calculations have been used to study the adsorption geometry and reaction pathways of biomass-derivatives or their probe molecules on single crystal metal surfaces [13,20-23]. Vorotnikov *et al.* [24] performed DFT calculations to investigate the reaction mechanisms and reaction barriers for the hydrogenation of furfural to 2-methylfuran, furfuryl

alcohol and furan on Pd(111). Myint *et al.* [25,26] compared the adsorption and reaction pathways of propanal and 1-propanol on Ni/Fe(111), Cu/Ni(111) and Ni/Mo(110) bimetallic surfaces using DFT calculations and temperature-programmed desorption (TPD). Similar theoretical and experimental studies have been carried out to study the hydrogenation of C=C bonds in a variety of molecules over the 3d/Pt(111) model surfaces and supported Pt-3d bimetallic catalysts [27-29]. These surface science experiments and DFT calculations provide insights into the reaction mechanisms and help the design of efficient hydrogenation catalysts.

This work reports the utilization of Pt-Ni and Pt-Co bimetallic catalysts for 2(5H)-furanone hydrogenation. DFT calculations and surface science experiments under ultrahigh vacuum (UHV) conditions were performed on the Ni/Pt(111) and Co/Pt(111) bimetallic surfaces as well as Pt(111), Ni(111) and Co(0001) monometallic surfaces to study the effect of bimetallic formation on the adsorption and hydrogenation of 2(5H)-furanone. In parallel, SiO₂-supported Pt-Ni and Pt-Co bimetallic catalysts and the corresponding monometallic catalysts were synthesized, characterized and evaluated for the liquid-phase hydrogenation of 2(5H)-furanone to GBL. The combination of theoretical and experimental studies provided a fundamental understanding of 2(5H)-furanone hydrogenation over bimetallic catalysts.

2. Theoretical and experimental methods

2.1 Density functional theory (DFT) calculations

All DFT calculations were performed using the Vienna *Ab-Initio* Simulation Package (VASP) code [30-33]. A plane wave cut-off energy of 400 eV and a $3 \times 3 \times 1$ Monkhorst-Pack grid were used for total energy calculations. The interactions between the electrons and nuclei were treated with all electron like projector augmented wave (PAW) potentials with the generalized gradient

approximation (GGA) using the PW91 functional [34,35].

The Pt(111), Ni(111) and Co(0001) monometallic surfaces and Pt-Ni-Pt(111), Ni-Pt-Pt(111), Pt-Co-Pt(111) and Co-Pt-Pt(111) bimetallic surfaces were modeled using four layers of 3×3 surface slabs. The Pt(111) surface was modified by replacing the subsurface (2nd layer) Pt atoms with Ni and Co atoms to model the Pt-Ni-Pt(111) and Pt-Co-Pt(111) subsurface structures, respectively. The Ni-Pt-Pt(111) and Co-Pt-Pt(111) surfaces were modeled by replacing the top Pt atoms of the Pt(111) surface with Ni and Co atoms, respectively. A vacuum layer of ~ 14 Å thick was added in the slab cell along the direction perpendicular to the surface in order to minimize the artificial interactions between the surface and its periodic images. During geometry optimization, atoms in the top two layers were allowed to relax while atoms in the bottom two layers were fixed until the Hellman-Feynman force on each ion was smaller than 0.01 eV/Å. The binding energy (BE) of an adsorbate was calculated as:

$$\text{BE(adsorbate)} = E(\text{slab} + \text{adsorbate}) - E(\text{slab}) - E(\text{adsorbate}) \quad (1)$$

where $E(\text{slab} + \text{adsorbate})$, $E(\text{slab})$ and $E(\text{adsorbate})$ are the total energy of slab with adsorbate, energy of clean slab and energy of adsorbate in the gas phase, respectively. The transition state of a chemical reaction in this work was located using the climbing image nudged elastic band (CI-NEB) method [36]. The activation energy (E_a) of a chemical reaction is defined as the energy difference between the initial and transition states while the reaction energy (ΔE) is defined as the energy difference between the initial and final states.

2.2 Temperature-programmed desorption (TPD) experiments

The TPD experiments were performed in a UHV chamber with a base pressure of 1×10^{-10} Torr, equipped with an Auger electron spectroscopy (AES), a mass spectrometer, a sputter gun and

the Ni (or Co) metal source, as described previously [37]. A Pt(111) single crystal (Princeton Scientific, 99.99%, 2 mm thick and 10 mm in diameter) was placed in 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 Pt(111) sample for temperature measurement. The Pt(111) surface was cleaned using sputtering-annealing cycles. The Ni/Pt(111) and Co/Pt(111) bimetallic surfaces were prepared by controlling the current of Ni or Co metal source, the temperature of Pt(111) surface and the deposition time. In this work, the Ni-terminated and Co-terminated bimetallic surfaces, Ni-Pt-Pt(111) and Co-Pt-Pt(111), were prepared by depositing a monolayer (ML) coverage of Ni and Co, respectively, with the Pt(111) substrate held at 300 K. The Pt-terminated bimetallic surfaces, Pt-Ni-Pt(111) and Pt-Co-Pt(111), were obtained by deposition with the Pt (111) substrate held at 600 K. The bimetallic surface composition was characterized using AES as described previously [38]. Longer deposition time generated surfaces composed of a Ni (or Co) film of increasing thickness on Pt(111), designated as thick Ni (or Co), which approximated the structure and reactivity of Ni(111) (or Co(0001)) [39].

2(5H)-Furanone (Sigma Aldrich, 98%) and GBL (Sigma Aldrich, 99%) were transferred into separate glass sample cylinders and purified using freeze-pump-thaw cycles. All other gases including hydrogen and neon 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. During the TPD measurements, the crystal surface with adsorbate was heated with a linear rate of $3\text{ K}\cdot\text{s}^{-1}$ and the products desorbing from the crystal surface were monitored using a quadrupole mass spectrometer.

2.3 Preparation of supported catalysts

The supported Pt-Ni and Pt-Co bimetallic catalysts were prepared by incipient wetness co-impregnation to obtain the greatest extent of bimetallic bond formation, as described previously [40]. The corresponding Pt, Ni and Co monometallic catalysts were also synthesized to serve as control samples. The metal loading for each catalyst was listed in **Table 1**. Typically, the respective metal precursors ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Alfa Aesar) were dissolved in a suitable amount of distilled water just sufficient to fill the pores of the SiO_2 support ($140 \text{ m}^2 \cdot \text{g}^{-1}$, Alfa Aesar), which was then dropwise added to the support. The impregnated samples were treated with ultrasound for 1 h to facilitate the metal dispersion. The catalysts were then dried at 353 K for 10 h and calcined in air at 723 K for 3 h.

2.4 Characterization of supported catalysts

The CO chemisorption measurements were performed on a Quantachrome ChemBET Pulsar TPR/TPD instrument equipped with a thermal conductivity detector (TCD) to estimate the number of metal active sites for the supported catalysts. For each test, 200 mg of catalyst was loaded into a U-tube quartz reactor and reduced in 10% H_2/He at 723 K for 1 h. The sample was then purged with pure He at 723 K for 30 min to remove the absorbed H_2 on the catalyst surface and cooled to room temperature. Subsequently, CO pulses were injected consecutively until the effluent area of the pulses was constant. The hydrogen temperature-programmed reduction (H_2 -TPR) measurements were carried out on the same apparatus to test the reducibility of the supported catalysts. The sample (~200 mg) was heated from room temperature to 1073 K at a ramp of $10 \text{ K} \cdot \text{min}^{-1}$ with a 5% H_2/Ar stream of $100 \text{ mL} \cdot \text{min}^{-1}$.

Transmission electron microscopy (TEM) images were taken on a JEM2010 transmission electron microscope at 200 kV. To prepare the TEM samples, the catalysts were first reduced in

hydrogen at 723 K for 3 h, which were then grinded into fine powders and suspended in acetone with a concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$. Droplets of the suspension were deposited onto the carbon coated copper grid and dried overnight at room temperature. For each catalyst, over 100 particles were collected to analyze the metal particle size distribution and to calculate the average metal particle size.

2.5 Catalytic evaluation of supported catalysts

The supported catalysts were evaluated for the liquid-phase hydrogenation of 2(5H)-furanone in a stainless steel autoclave (Weihai Chemical Machinery Co., Ltd., 300 mL). 2(5H)-Furanone was synthesized by furfural oxidation and purified by vacuum distillation as described in a previous publication [11]. The purity of the synthesized 2(5H)-furanone was in the range of 95-98%, which was determined with a gas chromatography (GC) by comparing the purified 2(5H)-furanone with the standard sample (98.0%, Alfa Aesar). In a typical experiment, the catalyst was reduced in H_2 at 723 K for 3 h and protected in N_2 in the reduction tube prior to the reaction. Then 6.0 g of 2(5H)-furanone, 100 mL of methanol (99.5%, Beijing Chemical Works) as the solvent, and 0.15 g of the reduced catalyst, were loaded into the reactor, which was sealed and purged with N_2 immediately and then heated to 353 K under 0.5 MPa H_2 . When the reaction temperature reached at the specified value (i.e. 353 K), the reactor was pressurized to 3.5 MPa within 5 min. The time when the pressure achieved at 3.5 MPa was considered as the zero of the reaction time. The stirring speed was set at $800 \text{ r}\cdot\text{min}^{-1}$ and the H_2 gas flow rate was set at $180 \text{ mL}\cdot\text{min}^{-1}$ to reduce the gas-liquid mass transfer resistance. The products were sampled and analyzed using a GC 7900 II (Techcomp Instrument Company) equipped with a super-wax capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.5 \text{ }\mu\text{m}$) and a flame ionization detector (FID). The

conversion of 2(5H)-furanone and selectivity to GBL were calculated as:

$$\text{Conversion of 2(5H)-furanone (\%)} = (n_{F,0} - n_F) / n_{F,0} \times 100 \quad (2)$$

$$\text{Selectivity to GBL (\%)} = n_G / (n_{F,0} - n_F) \times 100 \quad (3)$$

where $n_{F,0}$ is the initial mole of 2(5H)-furanone loaded into the reactor, and n_G and n_F are the moles of GBL and 2(5H)-furanone, respectively.

To estimate the apparent reaction rate constant (k_r), the 2(5H)-furanone concentration (C_F) was fitted as a function of the reaction time based on Equation (4) with the reaction order (p) fixed at 1.0. With the application of first-order law, the experimental data could be well described, with $R^2 > 0.98$, for all five catalysts.

$$dC_F/dt = k_r C_F^p \quad (4)$$

The initial turnover frequency (TOF) for the hydrogenation of 2(5H)-furanone to GBL was calculated as:

$$\text{TOF}_{\text{initial,GBL}} = (k_r \times n_{F,0}) / n_{\text{active sites}} \times S_{\text{initial,GBL}} \text{ s}^{-1} \quad (5)$$

where $S_{\text{initial,GBL}}$ is the initial selectivity to GBL obtained with the conversion of 2(5H)-furanone below 5%. The mole of metal active sites ($n_{\text{active sites}}$) was estimated by the CO chemisorption.

3. Results

3.1 DFT calculations

DFT calculations were carried out to compare the adsorptions of 2(5H)-furanone and GBL on both the monometallic and bimetallic surfaces with a Ni or Co layer placed either in the surface or subsurface. The top and side views of the DFT optimized configurations of 2(5H)-furanone and GBL on the Pt(111) surface are displayed in **Figure 1**, showing that 2(5H)-furanone binds to the Pt(111) surface through C atoms that have only one C-H bond (**Figure 1(b)**), and that GBL

primarily binds through the O atom in the C=O bond (**Figure 1(c)**). The d-band centers of Pt(111), Ni(111), Co(0001), Pt-Ni-Pt(111), Ni-Pt-Pt(111), Pt-Co-Pt(111) and Co-Pt-Pt(111) surfaces and the binding energies of atomic H, 2(5H)-furanone and GBL on these seven surfaces are summarized in **Table 2**. It should be noted that when the subsurface layer of Pt(111) is replaced by either Ni or Co, the d-band of Pt is broadened and consequently the d-band center shifts away from the Fermi level. In contrast, the Ni-terminated and Co-terminated surfaces exhibit a d-band center closer to the Fermi level than Ni(111) and Co(0001), respectively. The binding energy of 2(5H)-furanone is less than -0.20 eV on Pt-Ni-Pt(111) and Pt-Co-Pt(111), while it increases to -1.65 and -1.71 eV on Ni-Pt-Pt(111) and Co-Pt-Pt(111), respectively. The binding energy of GBL on the three monometallic surfaces and two Pt-terminated bimetallic surfaces is similarly in the range of -0.20 ~ -0.40 eV, whereas it significantly increases to -1.08 and -1.22 eV on Ni-Pt-Pt(111) and Co-Pt-Pt(111), respectively.

The DFT calculated binding energies of atomic H, 2(5H)-furanone and GBL on different model surfaces are plotted against the corresponding surface d-band center in **Figure 2**. It appears that the binding energies of atomic H, 2(5H)-furanone and GBL generally decrease as the surface d-band center shifts away from the Fermi level, which is consistent with the d-band model proposed by Nørskov and Hammer [41,42].

3.2 TPD results

TPD experiments of 2(5H)-furanone hydrogenation were performed on the hydrogen pre-dosed Pt(111), Ni/Pt(111), Co/Pt(111), thick Ni and thick Co surfaces. The TPD spectra of the desorbing gas phase species, 2(5H)-furanone ($m/e = 55$) and GBL ($m/e = 86$), are shown in **Figure 3**. As shown in **Figure 3(a)**, a desorption peak of 2(5H)-furanone is observed at 200 K for all the

surfaces, which is assigned to the physisorbed 2(5H)-furanone. For the Pt-Ni-Pt(111) and Pt-Co-Pt(111) surfaces, the detection of another desorption peak from the chemisorbed 2(5H)-furanone at 257 K suggests that less amount of 2(5H)-furanone is involved in the subsequent reaction on these two surfaces. **Figure 3(b)** compares the spectra of GBL on various surfaces. It shows that a large amount of GBL desorbs from the Ni-Pt-Pt(111) surface at 282 K, and Co-Pt-Pt(111) surface also exhibits activity for the production of GBL. However, almost no GBL is detected from the Pt-Ni-Pt(111) and Pt-Co-Pt(111) surfaces, because 2(5H)-furanone might desorb from the surface before its hydrogenation. For monometallic surfaces, the thick Ni surface is found to be active for 2(5H)-furanone hydrogenation to GBL, while the thick Co and Pt(111) surfaces show no activity for the production of GBL.

The yield of GBL from the TPD measurements was determined by the following equation:

$$\text{Yield of } \text{C}_4\text{H}_6\text{O}_2 = \left(\theta_{\text{CO}}^{\text{sat}} / P_{\text{CO}}^{\text{sat}} \right) \times P_{\text{C}_4\text{H}_6\text{O}_2}^{\text{C}_4\text{H}_4\text{O}_2} \times \left(S_{28 \text{ amu}}^{\text{CO}} / S_{86 \text{ amu}}^{\text{C}_4\text{H}_6\text{O}_2} \right) \quad (6)$$

The $S_{86 \text{ amu}}^{\text{C}_4\text{H}_6\text{O}_2}$ and $S_{28 \text{ amu}}^{\text{CO}}$ are mass spectrometer sensitivities for GBL (86 amu) and CO (28 amu), respectively. The $P_{\text{C}_4\text{H}_6\text{O}_2}^{\text{C}_4\text{H}_4\text{O}_2}$ is the peak area of GBL from 2(5H)-furanone hydrogenation. The $P_{\text{CO}}^{\text{sat}}$ is the peak area of CO from the saturated CO adsorption on Pt(111) and $\theta_{\text{CO}}^{\text{sat}}$ is the saturation coverage of CO (0.68 ML) on Pt(111) [43]. The yield of GBL was determined by comparing the mass spectrometer sensitivity factors of GBL and CO at equal background concentrations of GBL and CO. The yield of CO was obtained by comparing its TPD peak area with that after saturation exposure of CO on the Pt(111) surface. **Table 3** summarizes the calculated yields of GBL from all the surfaces. The Ni (or Co)-Pt-Pt(111) surface exhibits a higher yield of GBL than that from either Pt(111) or thick Ni (or Co) surface, suggesting that the bimetallic formation enhances the hydrogenation of 2(5H)-furanone to GBL. Additionally, only a

small amount of GBL is produced from the Pt-Ni-Pt(111) and Pt-Co-Pt(111) surfaces, as the majority of the chemisorbed 2(5H)-furanone desorbs at 257 K from these two surfaces. Other undesired decomposition products such as CO and propane were also observed in the TPD experiments, which were not discussed in this paper due to the different reaction environments between the UHV and autoclave experiments.

3.3 Characterization of supported catalysts

The CO chemisorption was employed to estimate the number of metal active sites for the SiO₂-supported catalysts. The results are summarized in **Table 1**. The CO uptake values are 3.9, 3.6 and 3.1 $\mu\text{mol}\cdot\text{g}^{-1}$ for Pt/SiO₂, Ni/SiO₂ and Co/SiO₂, respectively. The introduction of Ni into Pt increases the CO uptake value to 4.8 $\mu\text{mol}\cdot\text{g}^{-1}$. However, the addition of Co to Pt does not significantly increase the CO binding sites and a CO uptake value of 4.0 $\mu\text{mol}\cdot\text{g}^{-1}$ is obtained.

The TEM images and metal particle size distributions are shown in **Figure 4**, and the average metal particle sizes are listed in **Table 1**. For the Pt/SiO₂ monometallic catalyst, the metal particles mainly span the range of 1-6 nm with an average particle size of 2.7 nm. After the addition of Ni and Co, the metal particle sizes are still distributed in a similar range, but the average metal particle sizes slightly increase to 3.4 and 4.0 nm, respectively. In comparison, the other two monometallic catalysts, Ni/SiO₂ and Co/SiO₂, have much broader metal particle size distributions and larger average metal particle sizes.

Figure 5 shows the H₂-TPR profiles of SiO₂-supported catalysts. Two reduction peaks at 449 K and 692 K are observed for Pt/SiO₂. The appearance of two H₂ consumption peaks for Pt was reported by Augustine for Pt/Al₂O₃ [44], suggesting that they were caused by the reduction of two-dimensional PtO₂ and three-dimensional platinum oxide. The Ni/SiO₂ exhibits a main

reduction peak of NiO at 746 K. The Pt-Ni/SiO₂ bimetallic catalyst is reduced at a much lower temperature than Ni/SiO₂, as it exhibits a narrow and intense reduction peak at 560 K. For Co/SiO₂, the first reduction peak at 630 K is assigned to the reduction of Co₃O₄ to CoO and the prolonged shoulder peak in the range of 725-867 K is caused by the subsequent reduction of CoO to metallic Co [45]. For the Pt-Co/SiO₂ bimetallic catalyst, the two reduction peaks decrease to 483 K and 554 K, respectively. Although the reduction temperatures of Pt-Ni/SiO₂ and Pt-Co/SiO₂ are higher than that of Pt/SiO₂, these three Pt-based catalysts can be completely reduced below 723 K, at which temperature the catalysts were reduced before their catalytic evaluations.

3.4 Catalytic evaluation of supported catalysts

The SiO₂-supported catalysts were evaluated in the liquid-phase hydrogenation of 2(5H)-furanone under the same reaction conditions. As shown in **Figure 6(a)**, the selectivity to GBL over each tested catalyst is plotted as a function of 2(5H)-furanone conversion. The results show that for all five SiO₂-supported catalysts, the selectivity to GBL gradually decreases with increasing conversion of 2(5H)-furanone. For example, with the conversion below 5%, the selectivity to GBL over Pt/SiO₂ is approximately 80%, while it decreases to 65.5% at a 2(5H)-furanone conversion of 100%. For the monometallic catalysts, Ni/SiO₂ is more selective for the production of GBL than Pt/SiO₂ and Co/SiO₂. The Pt-Ni/SiO₂ bimetallic catalyst shows a higher selectivity to GBL than both Pt/SiO₂ and Ni/SiO₂, indicating that the addition of Ni to Pt promotes the hydrogenation of the C=C bond. Similarly, the Pt-Co/SiO₂ bimetallic catalyst is also more selective to GBL than Pt/SiO₂ and Co/SiO₂. As summarized in **Table 4**, the final selectivity to GBL is 77.5% over Pt-Ni/SiO₂ and 71.3% over Pt-Co/SiO₂. In addition to GBL, side products including 2-hydroxytetrahydrofuran due to the hydrogenation of the C=O bond, and methyl

butyrate and butanediol due to the ring opening reactions were also detected with trace amounts in the reaction. The poor carbon balance of the products (<80%) was most likely caused by the self-polymerization of 2(5H)-furanone, and the polymerizations between 2(5H)-furanone and other products existing in the reaction system.

To make a quantitative comparison for catalyst activity, the reaction rate constants are quantified by fitting a first-order rate law to the consumption of 2(5H)-furanone, as presented in **Table 4**. The reaction rate constants over Pt/SiO₂ (0.006 min⁻¹) and Ni/SiO₂ (0.005 min⁻¹) are similar, while Co/SiO₂ is less active with a reaction rate constant of 0.002 min⁻¹. The addition of Ni and Co to Pt increases the reaction rate constant to 0.021 min⁻¹ and 0.012 min⁻¹, respectively, significantly higher than that over the corresponding monometallic catalysts. To further discuss the catalyst activity for the production of GBL, the initial TOFs for the hydrogenation of 2(5H)-furanone to GBL over the SiO₂-supported catalysts are calculated and listed in **Table 4**. The TOF values over Pt/SiO₂, Ni/SiO₂ and Co/SiO₂ are 10.5, 9.7 and 4.5 s⁻¹, respectively. Note that because the initial selectivity to GBL is used in Equation (5), the absolute TOF values are not identical to those in our previous work [11], but the trend of TOF among the three SiO₂-supported monometallic catalysts is the same. For the Pt-Ni/SiO₂ and Pt-Co/SiO₂ bimetallic catalysts, the TOF for the hydrogenation of 2(5H)-furanone to GBL is determined to be 30.9 and 18.5 s⁻¹, respectively. As the number of metal active sites was estimated by the CO chemisorption with the assumption that each absorbed CO molecule corresponded to one metal active site, the resulting TOFs were the average values.

In our previous work, the TOF for 2(5H)-furanone hydrogenation over a series of monometallic catalysts showed a volcano-type dependence on the d-band center, with Pd having

the highest activity. Based on this volcano-type relationship between TOF and d-band center, the Pt-Ni (or Co) bimetallic catalyst should be less active than Pt and Ni (or Co). However, this is obviously inconsistent with the current observation as the two bimetallic catalysts do exhibit significantly enhanced activities, indicating that the d-band center alone is not a sufficient descriptor for the catalyst activity for bimetallic catalysts. Therefore it is necessary to further discuss the bimetallic effect based on the TPD and DFT results. In general, the catalyst activity follows the trend of $\text{Pt-Ni/SiO}_2 > \text{Pt-Co/SiO}_2 > \text{Pt/SiO}_2 > \text{Ni/SiO}_2 > \text{Co/SiO}_2$, while the final selectivity to GBL shows the trend of $\text{Pt-Ni/SiO}_2 > \text{Ni/SiO}_2 > \text{Pt-Co/SiO}_2 > \text{Co/SiO}_2 > \text{Pt/SiO}_2$, as illustrated in **Figure 6(b)**.

4. Discussion

The results above demonstrate that Pt-Ni and Pt-Co bimetallic catalysts are more active for the selective hydrogenation of 2(5H)-furanone to GBL than the corresponding monometallic catalysts. The enhanced hydrogenation activities of the bimetallic catalysts are further discussed in this section by several correlations between the model surfaces and supported catalysts. In the TPD experiments, both the Ni-Pt-Pt(111) and Co-Pt-Pt(111) bimetallic surfaces with Ni or Co on the top layer exhibit a higher yield of GBL than the corresponding monometallic surfaces. According to the DFT calculations, the binding energy of 2(5H)-furanone is significantly higher on Ni-Pt-Pt(111) and Co-Pt-Pt(111) than that on the other surfaces. In addition, the binding energy of GBL is lower than that of 2(5H)-furanone on the same surface. In contrast, both the Pt-terminated bimetallic surfaces, Pt-Ni-Pt(111) and Pt-Co-Pt(111), are found to be almost inactive for the production of GBL in the TPD experiments. This is consistent with the DFT calculations, which shows that the binding of 2(5H)-furanone on the two subsurface structures is too weak,

leading to desorption of 2(5H)-furanone from the surface before hydrogenation reaction. However, correlating the GBL yield from 2(5H)-furanone hydrogenation in the TPD experiments with respect to the DFT calculated binding energy of 2(5H)-furanone on all seven model surfaces results in a poor correlation, as shown in **Figure 7(a)**. This result suggests that neither the binding energy of 2(5H)-furanone nor the surface d-band center alone is a sufficient descriptor for the hydrogenation activity when both monometallic and bimetallic surfaces are included in the current study.

Further DFT calculations were performed to estimate the activation energy (E_a) and reaction energy (ΔE) of elementary steps in the selective hydrogenation of 2(5H)-furanone to GBL on the most active surface, Ni-Pt-Pt(111), and the unmodified Pt(111) as a reference. The results are displayed in **Table 5**, which shows that the hydrogenation of 2(5H)-furanone to the $C_4H_5O_2$ intermediate on Pt(111) has $E_a = 0.65$ eV and $\Delta E = -0.13$ eV. Further hydrogenation of $C_4H_5O_2$ to GBL on Pt(111) has $E_a = 1.00$ eV and $\Delta E = 0.01$ eV. It is noted that the desorption energy of 2(5H)-furanone (0.73 eV) (**Table 2**) is comparable to the E_a (0.65 eV) of its hydrogenation to $C_4H_5O_2$. Thus 2(5H)-furanone desorption is kinetically competing with 2(5H)-furanone hydrogenation. However, entropy contribution at experimental reaction conditions significantly favors the desorption of 2(5H)-furanone over its hydrogenation. On Ni-Pt-Pt(111), the hydrogenation of 2(5H)-furanone to $C_4H_5O_2$ and $C_4H_5O_2$ to GBL has $E_a = 0.80$ eV, $\Delta E = 0.26$ eV and $E_a = 0.58$ eV, $\Delta E = 0.17$ eV, respectively. The E_a (0.80 eV) of 2(5H)-furanone hydrogenation to $C_4H_5O_2$ on Ni-Pt-Pt(111) is significantly lower than its desorption energy (1.65 eV). As a result, 2(5H)-furanone hydrogenation is kinetically competing with 2(5H)-furanone desorption even after including the entropy contribution. Furthermore, it is found that the E_a of the rate-determining

hydrogenation step ($*C_4H_5O_2 + *H \rightarrow *C_4H_6O_2$ on Pt(111) and $*C_4H_4O_2 + *H \rightarrow *C_4H_5O_2$ on Ni-Pt-Pt(111)) is lower on Ni-Pt-Pt(111) than on Pt(111). Thus the DFT results predict a higher activity of Ni-Pt-Pt(111) compared to Pt(111) for the selective hydrogenation of 2(5H)-furanone to GBL, in agreement with the corresponding TPD measurements.

The DFT and TPD predictions on model surfaces are validated by the catalytic evaluation of SiO₂-supported catalysts, where the initial TOFs of Pt-Ni/SiO₂ and Pt-Co/SiO₂ are higher than that of Pt/SiO₂. **Figure 7(b)** displays the correlation of the initial TOF for 2(5H)-furanone hydrogenation to GBL over SiO₂-supported Pt, Pt-Ni and Pt-Co catalysts with the hydrogenation activity of 2(5H)-furanone to GBL on Pt(111), Ni-Pt-Pt(111) and Co-Pt-Pt(111) model surfaces from TPD experiments. The nearly linear relationship demonstrates an excellent correlation between the model surfaces and supported catalysts. It should be noted that the Pt/SiO₂ monometallic catalyst does show activity for hydrogenation of 2(5H)-furanone to GBL in the catalytic evaluations, whereas no GBL is detected from the Pt(111) surface in TPD experiments. This inconsistency between the Pt(111) model surface and the supported Pt/SiO₂ catalyst is probably due to the differences between the UHV-TPD experimental conditions and the high-pressure reactor evaluation conditions.

The correlation between the model surfaces and supported catalysts suggests that the enhanced hydrogenation activity of the supported Pt-Ni bimetallic catalyst is likely due to the presence of a Ni-terminated surface structure. Previous DFT calculations and UHV experiments over model Ni/Pt(111) surfaces [46,47] indicated that the surface termination could change depending on the nature of the adsorbates. In addition, in a previous study using in-situ EXAFS [48] over supported Pt-Ni bimetallic catalysts for the reaction with ethylene glycol, the catalysts

changed from a Pt-terminated surface after H₂ reduction to mainly Ni-terminated surface after the introduction of ethylene glycol. In the current study, the hydrogenation reaction was carried out using methanol as the solvent, and both the reactants and products contained oxygen atoms, suggesting the possibility of the presence of Ni-terminated bimetallic structure. In-situ EXAFS studies are needed to determine the surface termination of the bimetallic catalysts under reaction conditions.

5. Conclusions

The selective hydrogenation of biomass-derived 2(5H)-furanone has been investigated by the combined DFT, surface science and reactor studies. Based on the results and discussion presented above, the following conclusions could be made: (1) TPD results show that the Ni (or Co)-Pt-Pt(111) bimetallic surface is more active than its monometallic counterparts; (2) DFT calculations confirm the higher hydrogenation activity on Ni-Pt-Pt(111), as the E_a of the hydrogenation step is lower on Ni-Pt-Pt(111) than on Pt(111); (3) The reactor studies show that the Pt-Ni/SiO₂ and Pt-Co/SiO₂ bimetallic catalysts are much more active than the corresponding monometallic catalysts, and the introduction of Ni and Co into Pt also improves the selectivity to GBL; (4) The good correlation between model surfaces and supported catalysts demonstrates the feasibility of employing this combined approach to guide the design of bimetallic catalysts for 2(5H)-furanone hydrogenation.

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References

- [1] R.A. Sheldon, *Green Chem.* 16 (2014) 950.
- [2] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, *Chem. Soc. Rev.* 41 (2012) 8075.
- [3] S. Shi, H. Guo, G. Yin, *Catal Commun.* 12 (2011) 731.
- [4] H. Choudhary, S. Nishimura, K. Ebitani, *Appl. Catal. A: Gen.* 458 (2013) 55.
- [5] L.A. Badovskaya, V.M. Latashko, V.V. Poskonin, E.P. Grunskaya, Z.I. Tyukhteneva, S.G. Rudakova, S.A. Pestunova, A.V. Sarkisyan, *J. Heterocycl. Chem.* 38 (2002) 1040.
- [6] J.P. Lange, E. van der Heide, J. van Buijtenen, R. Price, *ChemSusChem* 5 (2012) 150.
- [7] X. Li, X. Lan, T. Wang, *Catal Today* (2016), <http://dx.doi.org/10.1016/j.cattod.2015.11.036>
- [8] A. Hashmen, E. Kleinpeter, *Adv. Heterocycl. Chem.* 81 (2001) 107.
- [9] N. Ichikawa, S. Sato, R. Takahashi, T. Sodesawa, K. Inui, *J. Mol. Catal. A: Chem.* 21 (2004) 197.
- [10] S. Fernando, S. Adhikari, C. Chandrapal, N. Murali, *Energy Fuels* 20 (2006) 1727.
- [11] X. Li, X. Lan, T. Wang, *Green Chem.* 8 (2016) 638.
- [12] S. Zafeiratos, S. Piccinin, D. Teschner, *Catal. Sci. Technol.* 2 (2012) 1787.
- [13] W. Yu, M.D. Porosoff, J.G. Chen, *Chem. Rev.* 112 (2012) 5780.
- [14] J.A. Rodriguez, *Surf. Sci. Rep.* 24 (1996) 223.
- [15] S. Lu, W.W. Lonergan, J.P. Bosco, S. Wang, Y. Zhu, Y. Xie, J.G. Chen, *J. Catal.* 259 (2008) 260.

- [16] R. Zheng, M.D. Porosoff, J.L. Weiner, S. Lu, Y. Zhu, J.G. Chen, *Appl. Catal. A: Gen.* 419 (2012) 126.
- [17] J. Li, P. Tian, X. Wang, L. Shi, *Chem. Eng. J.* 175 (2011) 417.
- [18] U.R. Pillai, E. Sahle-Demessie, D. Young, *Appl. Catal. B: Environ.* 43 (2003) 131.
- [19] Q. Wang, H.Y. Cheng, R.X. Liu, J.M. Hao, Y.C. Yu, S.X. Cai, F.Y. Zhao, *Catal. Commun.* 10 (2009) 592.
- [20] S. Sitthisa, T. Sooknoi, Y. Ma, P.B. Balbuena, D.E. Resasco, *J. Catal.* 277 (2011) 1.
- [21] K. Xiong, W. Yu, D.V. Vlachos, J.G. Chen, *ChemCatChem* 7 (2015) 1402.
- [22] D.W. Goodman, *Ultramicroscopy* 34 (1990) 1.
- [23] J. Lee, Y. Xu, G.W. Huber, *Appl. Catal. B: Environ.* 140 (2013) 98.
- [24] V. Vorotnikov, G. Mpourmpakis, D.G. Vlachos, *ACS Catal.* 2 (2012) 2496.
- [25] M.N.Z. Myint, Y. Yan, J.G. Chen, *J. Phys. Chem. C* 118 (2014) 11340.
- [26] M.N.Z. Myint, J.G. Chen, *ACS Catal.* 5 (2015) 256.
- [27] H. Zhao, B.E. Koel, *J. Catal.* 234 (2005) 24.
- [28] S. Qi, W. Yu, W.W. Lonergan, B. Yan, J.G. Chen, *ChemCatChem* 2 (2012) 625.
- [29] S. Lu, W.W. Lonergan, Y. Zhu, Y. Xie, J.G. Chen, *Appl. Catal. B: Environ.* 91 (2009) 610.
- [30] C.M. Ammann, G.A. Meehl, W.M. Washington, C.S. Zender, *Geophys. Res. Lett.* 30 (2003) 1657.
- [31] G. Kresse, J. Furthmuller, *Phys. Rev. B* 54 (1996) 11169.
- [32] G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* 6 (1996) 15.
- [33] G. Kresse, J. Hafner, *Phys. Rev. B* 47 (1993) 558.
- [34] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais,

Phys. Rev. B 46 (1992) 6671.

- [35] M.P. Teter, M.C. Payne, D.C. Allan, Phys. Rev. B 40 (1989) 12255.
- [36] G. Henkelman, B.P. Uberuaga, H. Jonsson, J. Chem. Phys. 113 (2000) 9901.
- [37] A. Ruban, B. Hammer, P. Stoltze, H. L. Skriver, J. K. Nørskov, J. Mol. Catal. A: Chem. 115 (1997) 421.
- [38] W. Yu, M.A. Barteau, J.G. Chen, J. Am. Chem. Soc. 133 (2011) 20528.
- [39] N.A. Khan, H.H. Hwu, J.G. Chen, J. Catal. 205 (2002) 259.
- [40] W.W. Lonergan, D.G. Vlachos, J.G. Chen, J. Catal. 271 (2010) 239.
- [41] B. Hammer, J. K. Nørskov, Surf. Sci. 343 (1995) 211.
- [42] B. Hammer, O. H. Nielsen, J. K. Nørskov, Catal. Lett. 46 (1997) 31.
- [43] G. Ertl, M. Neumann, K. M. Streit, Surf. Sci. 64 (1977) 393.
- [44] S.M. Augustine, W.M.H. Sachtler, J. Catal. 116 (1989) 184.
- [45] M. Guo, G. Lu, React. Kinet. Mech. Cat. 113 (2014) 101.
- [46] C.A. Menning, J.G. Chen, J. Chem. Phys. 130 (2009) 174709.
- [47] C.A. Menning, H.H. Hwu, J.G. Chen, J. Phys. Chem. B 110 (2006) 15471.
- [48] S.A. Tupy, A.M. Karim, C. Bagia, W. Deng, Y. Huang, D.G. Vlachos, J.G. Chen, ACS Catal. 2 (2012) 2290.

Table captions

- Table 1** Catalyst composition, average metal particle size and CO uptake.
- Table 2** The d-band centers and binding energies of atomic H, 2(5H)-furanone ($C_4H_4O_2$) and GBL ($C_4H_6O_2$) on model surfaces.
- Table 3** Yield of GBL on metal surfaces from TPD measurements.
- Table 4** Catalytic performances of SiO_2 -supported catalysts.
- Table 5** Activation energies (E_a) and reaction energies (ΔE) of selective hydrogenation of 2(5H)-furanone ($C_4H_4O_2$) to GBL ($C_4H_6O_2$) on Pt(111) and Ni-Pt-Pt(111) surfaces.

Table 1 Catalyst composition, average metal particle size and CO uptake.

Entry	Catalyst ^a	Average metal particle size ^b	CO uptake
		(nm)	($\mu\text{mol}\cdot\text{g}^{-1}$)
1	0.5%Pt/SiO ₂	2.7	3.9
2	0.5%Ni/SiO ₂	4.6	3.6
3	0.5%Pt-0.5%Ni/SiO ₂	3.4	4.8
4	0.5%Co/SiO ₂	4.3	3.1
5	0.5%Pt-0.5%Co/SiO ₂	4.0	4.0

^a The SiO₂-supported catalysts were denoted as $x\%M_1$ - $y\%M_2$ /SiO₂, where x and y were the loadings in wt% of the supported metals.

^b The average metal particle size was determined by TEM.

Table 2 The d-band centers and binding energies of atomic H, 2(5H)-furanone ($C_4H_4O_2$) and GBL ($C_4H_6O_2$) on model surfaces.

Entry	Surface	d-band center (eV)	Binding energy (eV)		
			H	$C_4H_4O_2$	$C_4H_6O_2$
1	Pt(111)	-2.57	-2.75	-0.73	-0.28
2	Ni(111)	-1.45	-2.83	-0.49	-0.24
3	Co(0001)	-1.35	-2.78	-0.36	-0.30
4	Pt-Ni-Pt(111)	-2.75	-2.54	-0.19	-0.21
5	Ni-Pt-Pt(111)	-1.20	-3.02	-1.65	-1.08
6	Pt-Co-Pt(111)	-2.95	-2.40	-0.04	-0.23
7	Co-Pt-Pt(111)	-1.00	-3.01	-1.71	-1.22

Table 3 Yield of GBL on metal surfaces from TPD measurements.

Entry	Surface ^a	Yield of GBL (10 ⁻²)
1	Pt(111)	0.0
2	Ni(111)	6.8
3	Co(0001)	0.0
4	Pt-Ni-Pt(111)	1.0
5	Ni-Pt-Pt(111)	11.6
6	Pt-Co-Pt(111)	0.6
7	Co-Pt-Pt(111)	2.3

^a The TPD experiments were carried out on hydrogen pre-dosed metal surfaces.

Table 4 Catalytic performances of SiO₂-supported catalysts.

Entry	Catalyst ^a	k_r (10 ⁻² ·min ⁻¹) ^b	TOF (s ⁻¹)	Selectivity to GBL (%) ^c
1	Pt/SiO ₂	0.6	10.5	65.5
2	Ni/SiO ₂	0.5	9.7	71.6
3	Pt-Ni/SiO ₂	2.1	30.9	77.5
4	Co/SiO ₂	0.2	4.5	67.9
5	Pt-Co/SiO ₂	1.2	18.5	71.3

^a Reaction conditions: 2(5H)-furanone (6.0 g), catalyst (0.15 g), 100 mL of methanol as the solvent, 353 K, 3.5 MPa H₂, 180 mL·min⁻¹ H₂ gas flow, 800 rpm stirring.

^b The reaction order was assumed to be 1.0 with respect to 2(5H)-furanone.

^c The selectivity to GBL was calculated with 2(5H)-furanone just completely converted.

Table 5 Activation energies (E_a) and reaction energies (ΔE) of selective hydrogenation of 2(5H)-furanone ($C_4H_4O_2$) to GBL ($C_4H_6O_2$) on Pt(111) and Ni-Pt-Pt(111) surfaces.

Reaction ^a	Pt(111)		Ni-Pt-Pt(111)	
	E_a (eV)	ΔE (eV)	E_a (eV)	ΔE (eV)
$*C_4H_4O_2 + *H \rightarrow *C_4H_5O_2 + *$	0.65	-0.13	0.80	0.26
$*C_4H_5O_2 + *H \rightarrow *C_4H_6O_2 + *$	1.00	0.01	0.58	0.17

^a The surface species are denoted as *.

Figure captions

Fig. 1 Top (bottom) and side (top) views of DFT optimized geometries of (a) Pt(111) surface, (b) 2(5H)-furanone on Pt(111) surface and (c) GBL on Pt(111) surface.

Fig. 2 Binding energies of atomic H, 2(5H)-furanone ($C_4H_4O_4$) and GBL ($C_4H_6O_4$) vs surface d-band center for monometallic and bimetallic model surfaces.

Fig. 3 TPD spectra of (a) 2(5H)-furanone and (b) GBL following 4 L exposure of 2(5H)-furanone on metal surfaces.

Fig. 4 TEM images and metal particle size distributions of (a) Pt/SiO₂, (b) Ni/SiO₂, (c) Pt-Ni/SiO₂, (d) Co/SiO₂ and (e) Pt-Co/SiO₂.

Fig. 5 H₂-TPR profiles of the SiO₂-supported catalysts.

Fig. 6 Catalytic performances of the SiO₂-supported catalysts.

Fig. 7 Hydrogenation activity of 2(5H)-furanone to GBL from TPD experiments vs (a) DFT calculated binding energy of 2(5H)-furanone on model surfaces and (b) TOF over the SiO₂-supported catalysts.

Fig. 1 Top (bottom) and side (top) views of DFT optimized geometries of (a) Pt(111) surface, (b) 2(5H)-furanone on Pt(111) surface and (c) GBL on Pt(111) surface. Pt: light grey, O: red, C: brown and H: blue.

Fig. 2 Binding energies of atomic H, 2(5H)-furanone ($C_4H_4O_4$) and GBL ($C_4H_6O_4$) vs surface d-band center for monometallic and bimetallic model surfaces.

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