Computational Analysis of Byproduct Formation Pathways in Furfural Hydrogenation

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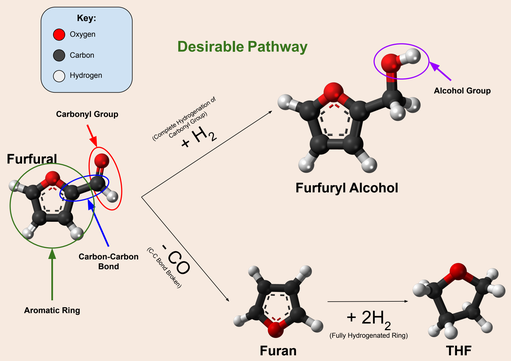
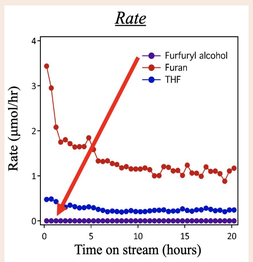
Introduction/Background

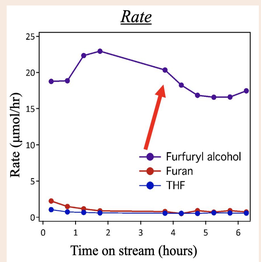
Furfuryl alcohol is an important molecule for synthesizing furan resins. These resins are generally used for coatings and adhesives due to their excellent heat stability and chemical resistance. Furfuryl alcohol is derived from Furfural through hydrogenation (adding hydrogen atoms to double bond). To produce furfuryl alcohol, we have to hydrogenate the carbonyl group (see figure). However, if hydrogenation breaks the carbon-carbon bond, undesirable compounds like furan and tetrahydrofuran (THF) are produced.



This reaction is typically carried out on a platinum surface due to its strong affinity for hydrogen atoms, which facilitates hydrogenation. However, the specific intermediates formed and the detailed transformation of furfural during the process remain not fully understood.



Hydrogenation on Pt(111)



Hydrogenation on PtSn

Research Goal

Our goal is to find out exactly how these undesirable products form by determining the most likely reaction pathway on an atomic scale. This could help us understand why these surface alloys are more effective catalysts for industrial furfuryl alcohol production.

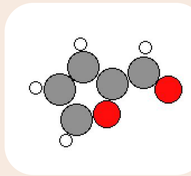
Methods

To determine the optimal reaction pathways, we used:

VASP computer modeling simulations.

We first used computer simulations to model the starting and ending molecules for each possible reaction. VASP adjusts each structure to find the lowest energy state. Because these simulations are done at near-zero temperature, we used the change in energy (ΔH) to estimate whether a reaction is thermodynamically favorable—only keeping reactions where the final state has lower energy than the starting one (ΔH < 0).

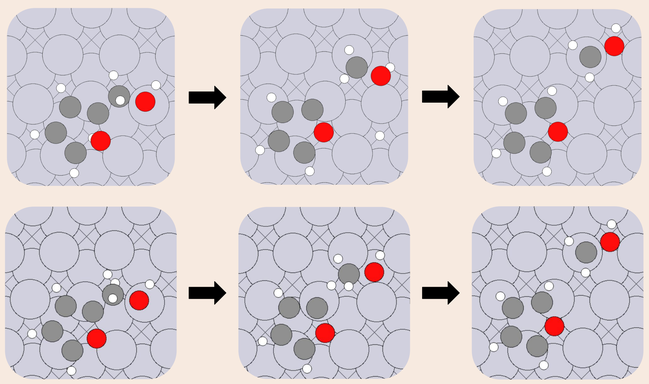
Next, we used another method (NEB simulation) to model how atoms move and bonds break or form during the reaction. This gave us an energy profile showing the activation energy, or how hard it is for the reaction to happen. Reactions with lower activation energy are more likely to occur, so we picked the most favorable pathway based on these results.



Furfural Molecule in VASP

Figures & Results

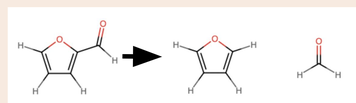
Platinum Surface Reaction Results



This was a an unreasonable reaction pathway to produce an undesirable product. In this reaction, we observe the **carbon-carbon bond** breaks first without interaction from the **hydrogen atom.** This causes a higher activation energy barrier (~2 eV) and therefore a lower probability of resulting in **Furan** and **CH_2OH**

This a similar but more plausible reaction pathway that produces an undesirable byproduct on Pt(111) surface. In this reaction, we start with **Furfuryl alcohol** and observe as a **hydrogen atom** on the surface disrupts the **carbon-carbon bond**, causing the molecule to split into **Furan** and **CH_2OH**

Platinum-Tin Alloy Surface Reaction Results

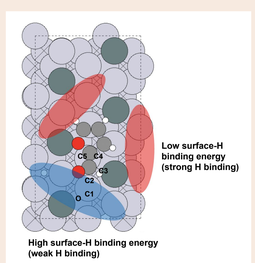


Formation of CH_2OH byproduct due to third step hydrogenation of furfural on Pt-Sn surfaces

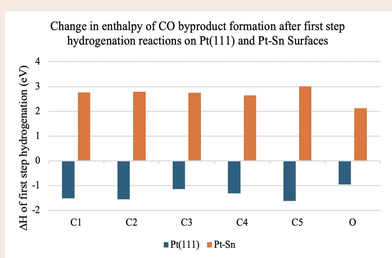
Different Surface-H Positions	Initial Energy (eV)	Final Energy (eV)	Change in Enthalpy (eV)
1	-748.97369	-750.070337	-1.096647
2	-749.985391	-750.070337	-0.084946
3	-750.028639	-750.070337	-0.041698
4	-749.987888	-750.070337	-0.082449
5	-750.026293	-750.070337	-0.044044

Formation of Furan and Formaldehyde byproduct due to second step hydrogenation of furfural on Pt-Sn surfaces

Different Hydrogen Positions	Initial Energy (eV)	Final Energy (eV)	Change in Enthalpy (eV)
C1 and surface-H on Pt	-745.927694	-746.28756	-0.359866
O and surface on Pt	-746.117555	-746.28756	-0.170005
C1 and surface-H on Sn	-745.190604	-746.28756	-1.096956
O and surface-H on Sn	-745.687169	-746.28756	-0.600391

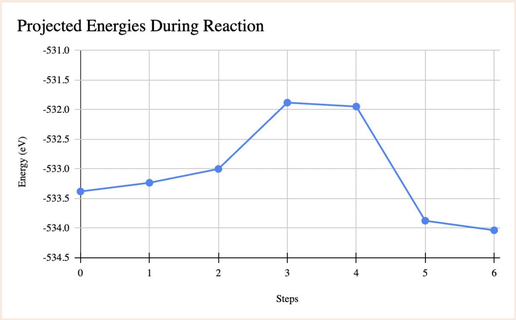


While formation of CO byproduct is thermodynamically favorable on Pt(111) surface, it is not on Pt-Sn surface; byproducts are readily formed on Pt(111) surface after first step hydrogenation. Also, carbonyl group is readily hydrogenated due to high H binding energy to Sn atoms of the surface alloy. Thus, selective formation of furfuryl alcohol is very favorable; byproducts formation is very unlikely in first step hydrogenation at the very least.



This graph shows the change in enthalpy for a reaction starting with a hydrogen on different initial locations on furfural and ending with CO and a hydrogenated furan ring. Because there is positive enthalpy on a Pt(111) surface and negative enthalpy on Pt-Sn surfaces, this shows that hydrogenation will not form CO on Pt-Sn surfaces

Conclusion



Here, the energy barrier is relatively low, and the process of breaking the carbon-carbon bond is aided by the surface hydrogen. This allows for a reaction with all steps happening simultaneously. However, on Pt–Sn surface alloys, the presence of Sn introduces a significant activation energy barrier (~2 eV). Sn changes the behavior of nearby platinum (Pt) atoms by donating electrons, which makes it harder for hydrogen atoms to stick to the surface. As a result, hydrogen is less likely to gather and move around near the active sites, helping prevent unwanted hydrogenation reactions.

Acknowledgments

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References

Chai, Wenrui. (2025). Selective Hydrogenation of Furfural on PtSn Alloy Surfaces. [Unpublished manuscript]

1. Corma, A., Iborra, S., Velty, A. Chem. Rev.: Chemical Routes for the Transformation of Biomass into Chemicals 107, 2411-2502 (2007). 2. Beniwal, S., Chai, W., Metavarayuth, K., et. al. J. Phys. Chem. C: Oxidation of Sn at the Cluster–Support Interface: Sn and Pt–Sn Clusters on TiO2(110) 125 (32), 17671-17683(2021). 3. Li, F., Ahsen, A. S., Ammal, S. C., et. al. Surf. Sci.: Characterizing the surface compositions of supported bimetallic PtSn clusters: effects of Cluster-Support interactions and surface adsorbates 751, 122623. (2024).