

# Understanding the Solvent and Particle Morphology Effects in Furfural Acetalization Reaction on Pd Nanostructures

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## Highlights

- Furfural dialkyl acetal formation from furfural on Pd catalyst was found to be facet-dependent.
- DFT calculated activation barriers were found to be low on Pd Cubes than on Pd Octahedras.
- Presence of explicit solvent molecules significantly dropped the activation barriers.
- Differential stabilization of transition states was observed due to proton shuttling via hydrogen bonded network.

## 1. Introduction

Heterogeneous catalysis is widely recognized for its structure-sensitive reactions where particle-size and shape of the nanoparticle can control the overall activity and selectivity (1). This arises due to the change in the fraction of surface atoms (viz terrace, corner or edge) (2). Moreover, solvent properties like polarity, basicity etc. also have a crucial impact on the catalytic activity. In this work, we have studied one such structure-sensitive acetalization reaction of biomass-derived furfural to produce an important biofuel. Furfural dialkyl acetal (FDA) have a high calorific value and high resistance to oxidation which makes it very valuable. With the help of density functional theory (DFT) simulations in presence of explicit solvent environment (methanol, ethanol, propanol, and butanol), we have tried to explain the mechanistic insights and correlate the experimental trends for furfural acetalization reaction over TiO<sub>2</sub> supported Pd nanostructures (cubes (100), octahedra (111) (Figure 1(i) and (ii)), and spheres (both (111) and (100)).

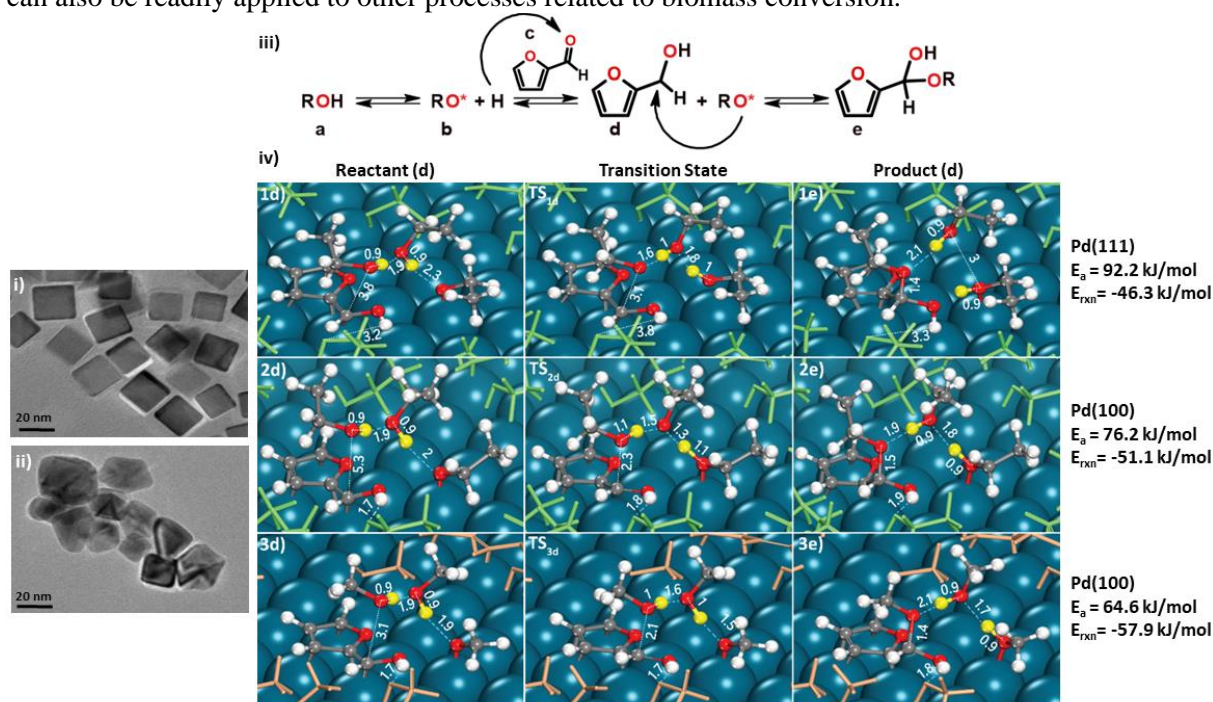
## 2. Methods

Pd octahedras and Pd cubes were synthesised using reported literature procedures (3-4). Synthesized catalysts were characterized by TEM, XRD and UV-Visible spectrophotometer. Acetalization reactions were carried out in a batch reactor and the products were analysed using GC. All the periodic, plane wave DFT calculations were implemented in Vienna *ab-initio* Simulation Package (VASP).

## 3. Results and discussion

Structure-dependent reactivity was observed for furfural conversion and acetal selectivity which followed a trend: Pd cubes (80% and 93%) > Pd octahedras (35% and 77%) > Pd spheres (41% and 75%) in ethanol solvent. Additionally, maximum conversion (90%) and acetal selectivity (100%) over Pd cubes was observed when the reaction was conducted with methanol as solvent. To get a detailed mechanistic insight into the reactivity towards furfural acetalization reaction at high coverage of solvents on two different Pd facets (100) and (111), DFT calculations were performed. As seen in Figure 1(iii), a three-step reaction mechanism was suggested: (i) alcohol hydroxyl-dehydrogenation; (ii) hydrogenation of furfural carbonyl oxygen; and (iii) generation of hemiacetal product. Among all the Pd facets, Pd (100) showed lower activation barriers (51.6, 26.7, and 76.2 kJ/mol) than Pd (111) surface

(78.6, 35.8, and 92.2 kJ/mol) in present of ethanol solvent (Figure 1(iv)). This is consistent with the experimental findings. The inclusion of methanol led to a further reduction in the activation barriers for the aforementioned steps on Pd (100) to 47.8, 23.9, and 64.6 kJ/mol, which explains the remarkable reactivity seen in the experiment. DFT simulations explained the role of the hydrogen bonding network between the solvent molecules and adsorbate for decreasing the activation barriers with the help of proton coupled-electron transfer. The ability to examine the intricacies of the solute-solvent interactions at the molecular level is made possible by our model's explicit handling of alcohol molecules, which can also be readily applied to other processes related to biomass conversion.



**Figure 1.** (i) TEM image: Pd (100) (~ 22 nm) and (ii) Pd (111) (~ 26 nm), (iii) Proposed reaction mechanism for hemiacetal formation, (iv) Reactant, transition, and product structures for hemiacetal formation in the presence of explicit ethanol solvent on Pd (111) (1d to 1e), Pd (100) (2d to 2e) and methanol on Pd (100): (3d to 3e). The O atom is displayed in red, C in gray, H in white and Pd in blue color. Few H taking part in the reaction is highlighted with yellow color and nearby ethanol and methanol molecules are shown in green and orange color respectively. Distances are marked in Å with white dashed lines and hydrogen bonds are shown with blue dashed lines.

#### 4. Conclusions

Furfural conversion and selectivity to furfural dialkyl acetal followed the trend: Pd (100) > Pd (111) > Pd(sphere). Pd (100) in presence of methanol as solvent displayed highest conversion and least activation barriers for furfural acetalization.

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#### Keywords

Furfural acetalization; facet-dependent reactivity; solvent effect; DFT simulations