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## THEORETICAL INSIGHT INTO THE SELECTIVITY OF GOLD, PALLADIUM AND PLATINIUM FOR HMF OXIDATION OVER DEGRADATION IN FDCA PRODUCTION

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### 1. Keywords

Biomass, Oxidation, Catalysis, DFT, Selectivity, Degradation

### 2. Highlights

- The impact of selected metals in improving FDCA yield was explored via molecular modelling.
- The ease of HMF oxidizing toward FDCA across different metals (Au, Pd & Pt) was accounted.
- The feasibility of HMF and HMFCa degradation (Fig 1) were explored.
- The best model to catalyze the oxidation of HMF into FDCA is identified as Au.

### 3. Purpose

FDCA production from HMF via base-free oxidation is known for being eco-friendly but suffers a lot of degradation challenges during its usage, especially at the initial stage [1,2]. Consequently, we seek insight into the thermodynamic feasibility of Au, Pd and Pt favouring the degradation of HMF and HMFCa into undesired products over the oxidation routes.

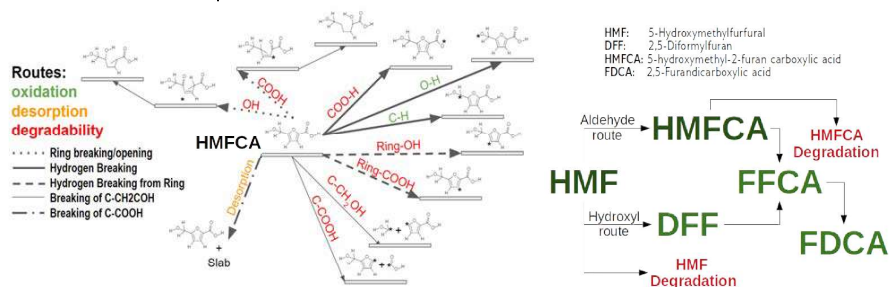


Figure 1: Scheme of the various HMFCa oxidation and degradation pathways (including full oxidation routes) explored.

### 4. Materials and methods / Computational Details

A thermodynamic feasibility study was deployed in understanding HMF oxidation and the routes leading to the degradation of HMF and HMFCa (Fig 1) into undesired products that compete selectively with the oxidation into FDCA. Periodic density functional theory calculations were performed using the VASP package to obtain energies. The exchange and correlation terms were obtained by the Perdew–Burke–Ernzerhof form of Generalized Gradient Approximation (GGA-PBE) functional similar to the one used in previous studies [3], using a cutoff of 400 eV. The Au, Pd and Pt (111) surface was modelled by a slab made of 4 layers using a dimension of 4x4 supercell. A Monkhorst-Pack mesh of 1x1x1 K point was used for the 2D Brillouin zone integration. The last 2 layers were frozen at the bulk-truncated positions (AuAu, PdPd, and PtPt interatomic distances of 2.93, 2.80 and 2.81 Å, respectively) while the first 2 layers were kept free to adjust. For geometry optimization, the convergence of the forces acting on atoms was 0.02 eV/Å.

## 5. Results and discussion

The activation of  $O_2$  in presence of water to yield hydroxyl was exothermic on Au (-0.38eV) and endothermic on Pt (0.57eV) and Pd (0.50eV) in Fig 2(a). The finding indicates that the presence of water would facilitate oxygen activation on Au compared to other metals. Across all metals studied, the aldehyde oxidation (CO-H) pathway was predicted to be more favourable for FDCA production than the hydroxyl oxidation pathway. HMFCFA was equally confirmed to be more stable than DFF across all the metals as shown in Fig 2(b). The findings of the study predict that HMF oxidation would favour HMFCFA more than DFF as an intermediate.

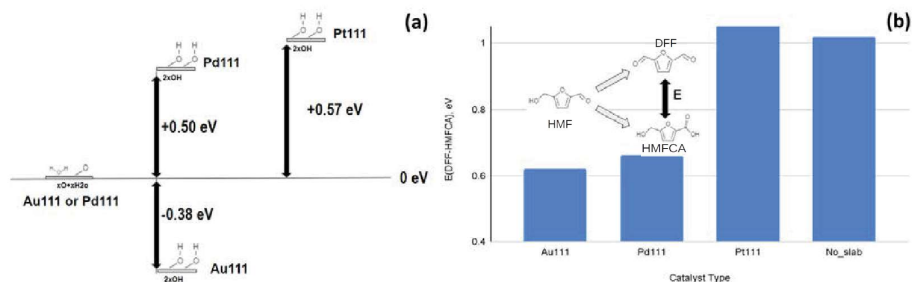


Figure 2: (a) Oxygen gas activation and (b) Energy difference (DFF-HMFCFA) across various metals.

Among the various HMF degradation routes studied, C-CH<sub>2</sub>OH breaking on all metals, and ring-opening on Au & Pd were feasible routes that easily degrade HMF during oxidation. A more intense degradation relative to the production of FDCA was predicted for Pd compared to Au and Pt. HMFCFA degradation study predicts C-CH<sub>2</sub>OH breaking across the metals would be significant compared to other degradation routes studied. The use of Pt prevents HMFCFA degradation while Pd eases the degradation of HMFCFA into undesired products. In contrast, Au is predicted to have shown the easiest routes for oxidizing HMFCFA to FDCA compared to other metals. The findings made were in agreement with the experimental report [2,4].

## 6. Conclusions and perspectives

The presence of water during oxygen activation was more favourable on Au, indicating a better activity compared to Pd and Pt. The aldehyde oxidation pathway was feasible for oxidizing HMF into FDCA. Pt was found to have shown a lesser potential for promoting HMF and HMFCFA degradation than others while Au was found to best oxidise HMF to HMFCFA and HMFCFA to FFCA. Insight from this study suggests the alloying [4] of the Au and Pt for the design of a new catalyst [3] that merges their complementary advantages of easing oxidation and hindering degradation of HMF during FDCA production.

## 7. References

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