Microkinetic study of selective glucose oxidation – monometallic or bimetallic catalyst?

Žan Lavrič[1 6], Janvit Teržan [1 2*], Ana Kroflič [1], Janez Zavašnik [3], Joanna Elżbieta Olszówka [4], Štefan Vajda [4], Matej Huš [1 5 6], Miha Grilc [1 6], Blaž Likozar [1 7]

1 Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

2 Department of Synthesis of Materials, Jožef Stefan Institute, Jamova Cesta 39, 1000 Ljubljana, Slovenia

3 Gaseous Electronics, Jožef Stefan Institute, Jamova Cesta 39, 1000 Ljubljana, Slovenia

4 Department of Nanocatalysis, J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Dolejškova 2155/3, CZ-182 23 Prague 8, Czech Republic

5 Institute for the Protection of Cultural Heritage of Slovenia (ZVKDS), Poljanska cesta 40, SI-1000 Ljubljana, Slovenia

6 University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia

7 Faculty of Polymer Technology, Ozare 19, SI-2380 Slovenj Gradec, Slovenia

**Janvit Teržan: Janvit.terzan@ki.si*

Highlights

- Oxygen adsorption was enhanced with the use of bimetallic catalysts
- The catalyst composition predicted by DFT was decisive for the balance of oxygen activation
- Kinetics from regression analysis *vs*. DFT kinetics
- The bimetallic AuPt/ZrO_2 catalyst showed the highest glucaric acid yield (32 %)

1. Introduction

The growth of our society, the limited availability of fossil fuels and the environmental impact of current industrial technologies have driven research into bio-based and renewable chemical feedstocks. Ever since, biomass conversion has gain increasing attention in the last two decades [1,2] due to incredible diversity of materials that can be obtained. One of the promising biomass-derived compounds is glucaric acid (GA) [3], which is currently obtained by nitric acid oxidation on an industrial level. However, this process is not ecological and alternative technologies are being explored. One of the most promising in the past two decades seems to be heterogeneous oxidation with the use of Au supported metallic catalyst in base free conditions [4]. However, the literature on the mechanism from glucose to GA is a lackluster, focusing only in the first step, towards gluconic acid. In this work, the investigation was focused on heterogeneous monometallic Au and bimetallic AuPt and AuCu catalysts, supported on ZrO_2. Main objectives were to determine the difference in activity towards selective glucose oxidation to GA, with mono- and bimetallic catalysts. Moreover, this is the first time, the whole pathway from glucose to GA was described. Each reaction step was also investigated with DFT calculations for comparison with experiments [5].

2. Methods

Catalysts were prepared by deposition precipitation method, where hydrazine hydrate was used as a reducing agent. The synthesized catalysts were analyzed by transmission electron microscopy (TEM), oxygen pulse chemisorption (OPS), X-ray diffraction (XRD) and X-ray photon spectroscopy (XPS) to determine the surface properties of the synthesized catalysts. Later, batch experiments were performed at different temperatures and oxygen partial pressures. Experimental data were used to build a

microkinetic model with predictive power. To connect the dots between experiments and kinetic studies, DFT calculations were performed.

3. Results and discussion

The catalyst analysis through XPS, TEM, and XRD confirmed alloy formation in bimetallic catalysts, revealing the presence of nano-sized Au crystallites in mixed AuPt and AuCu samples. DFT calculations indicated improved oxygen adsorption on Cu and Pt surfaces, correlating with enhanced catalytic activity. The study identified factors influencing the oxidation of glucose to gluconic acid (GU) and glucuronic acid (GA), emphasizing the importance of surface coverage and charge transfer. Bimetallic catalysts demonstrated higher GU production, and recyclability tests confirmed their stability over three cycles. In comparison to literature results, the bimetallic AuPt/ZrO_2 catalyst exhibited the highest GA yield under optimized conditions, highlighting its efficiency in the oxidation reaction.

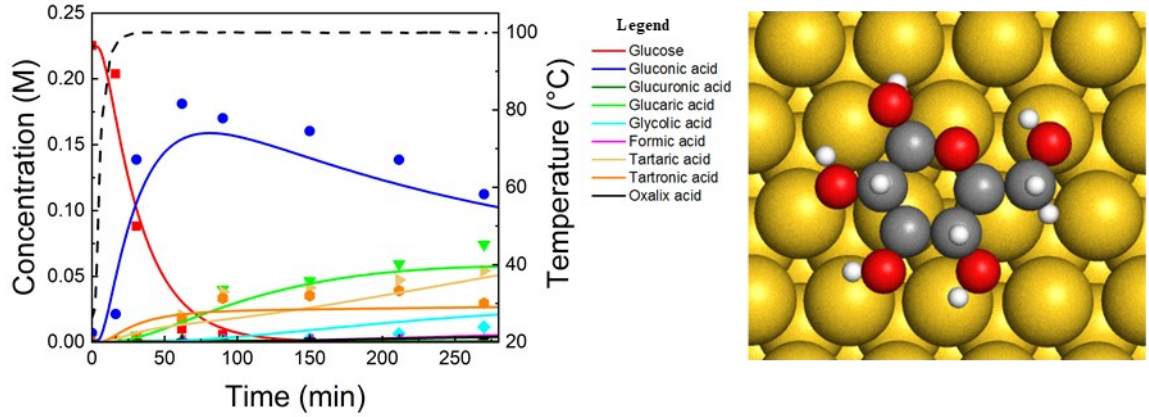

Figure 1. Oxidation experiment at 100 °C and 30 bar_g O_2 on AuPt/ZrO_2 catalyst (left). Top-down view of glucose ring on gold nanoparticle (right).

4. Conclusions

DFT calculations confirmed that the varied performance of Au, AuPt, and AuCu catalysts is attributed to differences in oxophilicity. The reaction dynamics hinge on the availability of oxygen species (O_2* and O*) provided by Pt and Cu, influencing reaction rates and selectivity. Microkinetic studies align with DFT results, showcasing the hindrance in glucose oxidation by pure Au and the enhanced selectivity of bimetallic AuPt. The study, integrating catalyst synthesis, characterization, DFT analysis, and microkinetic modeling, provides a foundational understanding for future research in biomass valorization and circular economy applications.

References

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Keywords
Glucaric acid; Glucose oxidation; Catalyst characterization; DFT; Microkinetic modelling