

Performance study of supported Au catalysts for the direct hydrogenation of CO₂ towards formic acid



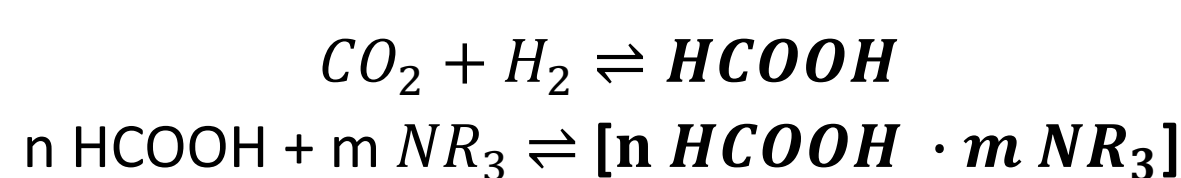
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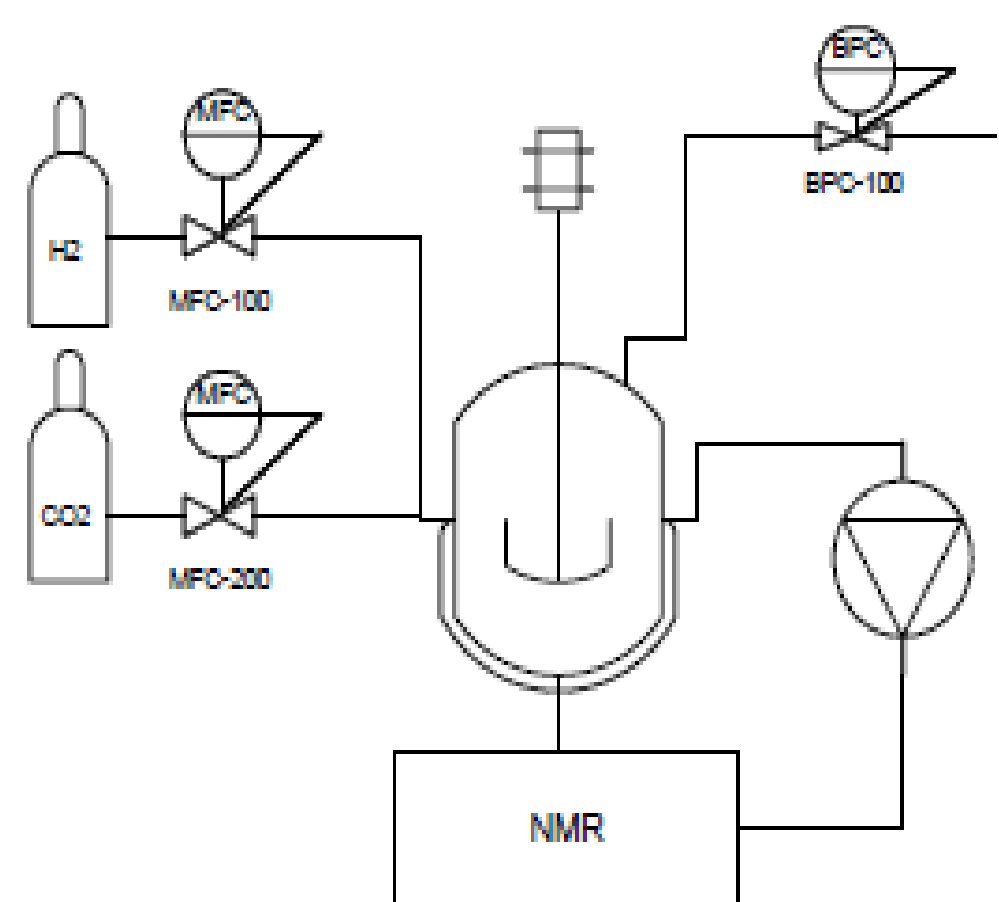
INTRODUCTION

Nowadays a major search is on the way to develop a method to transform CO₂ into valuable chemicals. One of these value-added products is **formic acid**, as it readily allows for a reversible transformation back to renewable hydrogen and CO₂, therefore acting as a method of **hydrogen storage**. Formic acid is known to store 4.3 wt% hydrogen and is liquid at ambient conditions, therefore allowing straightforward storage and transport. Due to the thermodynamic stability of the molecule, reduction strategies are employed based on trialkylamines leading to the formation of **adducts**.



Herein, we study the performance of Au supported catalyst the kinetics of formic acid and trialkylamine adduct formation, as well as the phase separation behavior of the products. To this end, the reaction is studied in a **batch reactor** using **inline NMR**.

Experimental set-up



Phase separation behavior

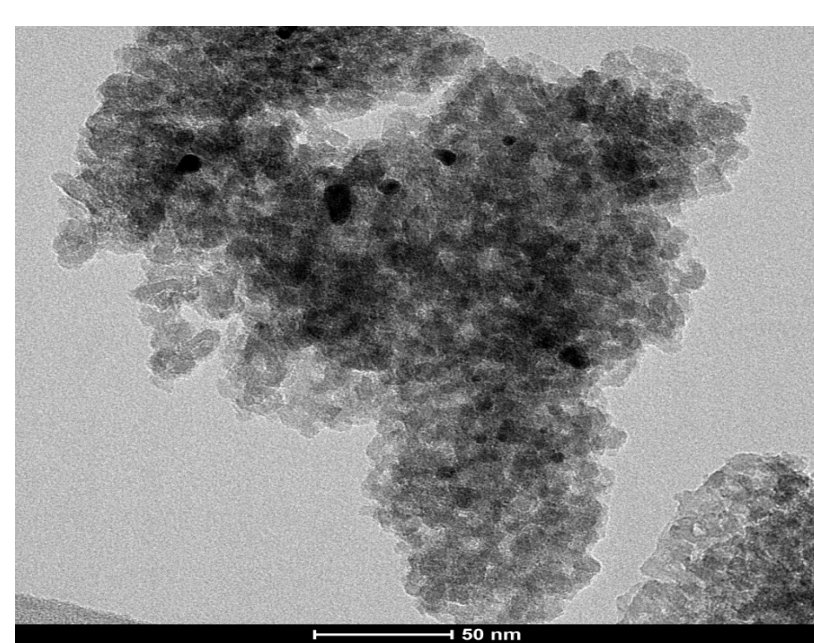
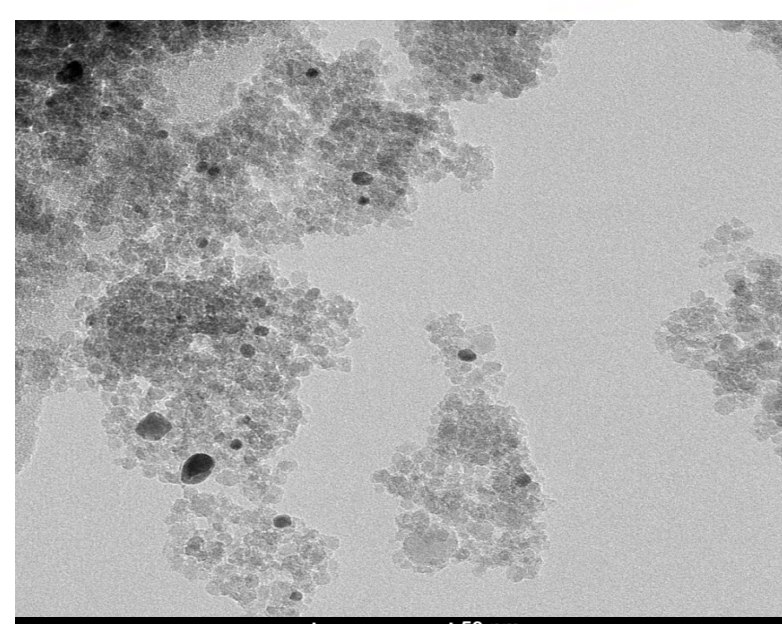
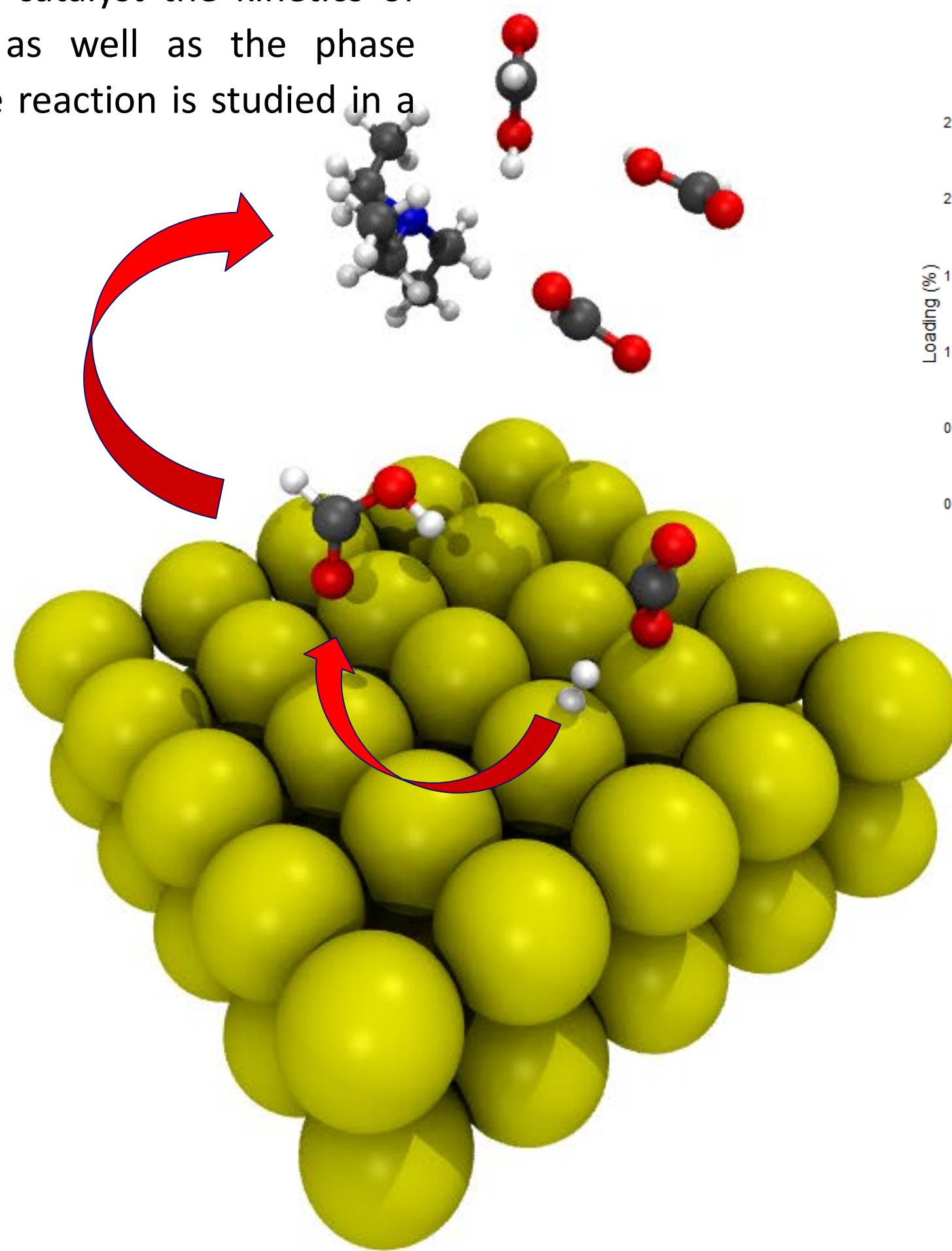
- Tertiary amine of any carbon length not miscible with adduct until a molar ratio of 1.5:1 FA:NR₃
- Due to inability of the amine to dissolve in the adduct and high adduct viscosity; the product cannot leave the catalyst
- Addition of solvent such as decanol removes biphasic nature, and leads to a significant improvement in kinetic performance from ppm level to 0.1 molar formic acid concentration



Biphasic nature of NR₃

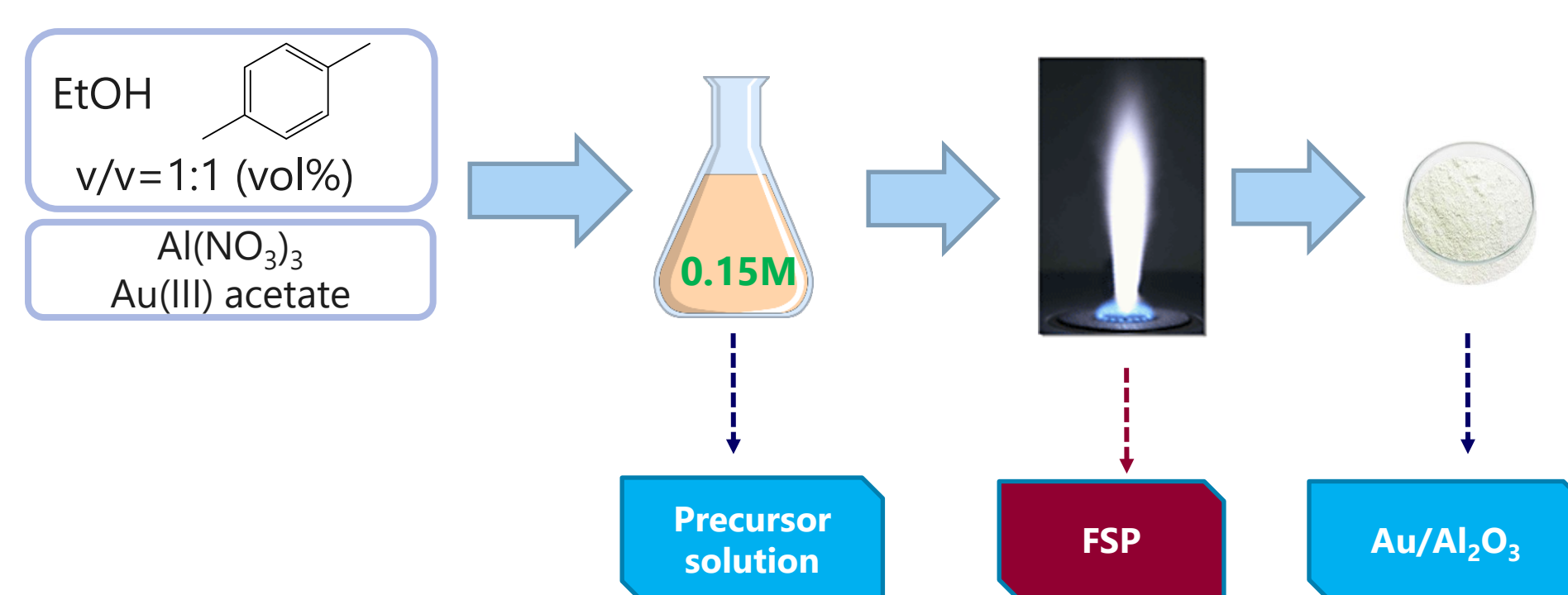


After the additional of decanol

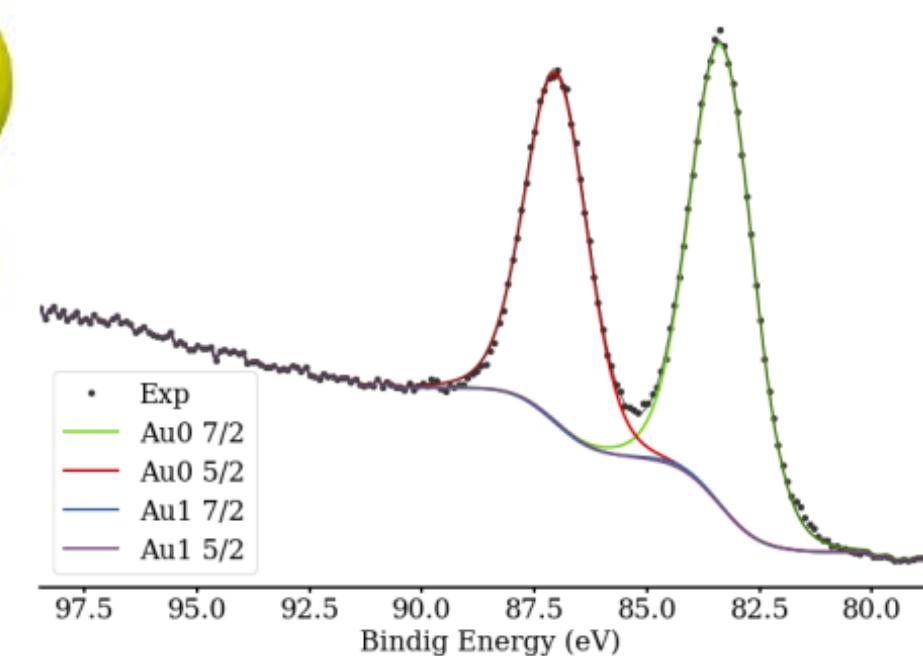
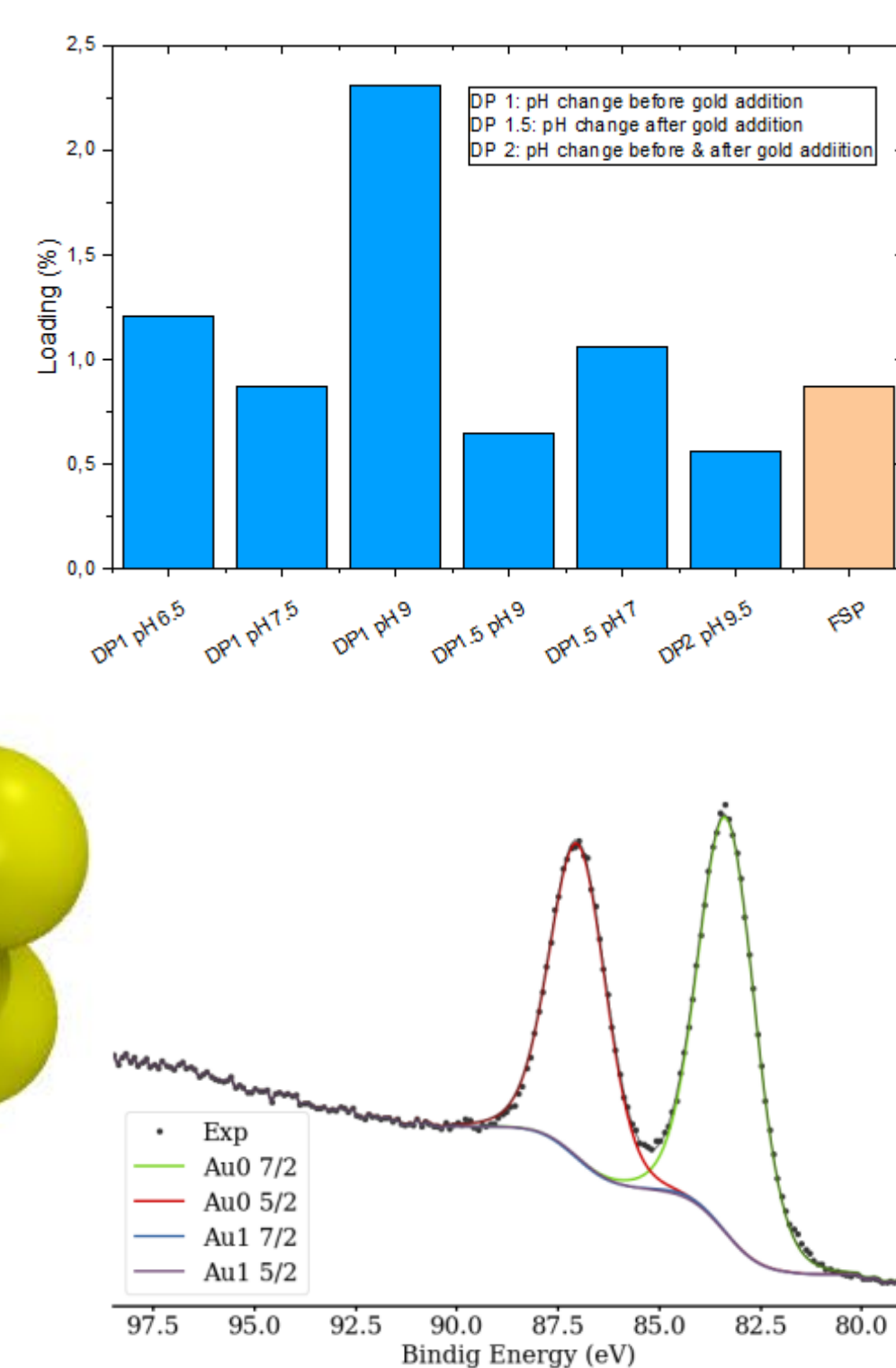


Preparation methods

- Deposition-precipitation (DP)
- One-step flame spray pyrolysis (FSP)



Results



- DP optimized
- Loading determined using ICP
- Residual chloride In support in case of FSP (confirmed by XPS)
- Main species: Au⁰
- Au⁰ confirmed active species by cyanide leaching

Conclusions and Outlook

- Au catalysts were prepared using deposition-precipitation and flame-spray pyrolysis
- The catalysts are currently studied at temperatures between 35-90°C and 10-20 bar using a 1:1 volume mixture of H₂ and CO₂ with tertiary amines as a reducing agent
- Theoretical studies based on DFT have shown the RLS to be hydrogen splitting and that the main active sites are nanoparticles < 2 nm
- Bimetallic Au based (combined with Ni, Pd and Ru) catalysts will be prepared using deposition-precipitation and flame-spray pyrolysis

