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## Platinum supported on Titania/C Dual-function Hybrid Support Catalysts for Electrocatalytic Reduction of Benzaldehyde

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### Introduction

The production of renewable, cleaner and affordable energy from biomass is one of the key solutions to global energy and environmental challenges. Selective hydrogenation of biomass-derived platform molecules is one of the most important biorefinery processes, however, is also the most capital and energy intensive step. Electrocatalytic reduction (ECR) is a new promising technology for this step, as it does not require molecular H<sub>2</sub>, can be performed under ambient conditions and required electric energy can be provided from renewable energy sources such as solar and wind energy. ECR technology still needs to overcome the limitations of optimum catalyst and reactor design, and establish fundamental understanding of kinetics, and reaction mechanism in presence of electric potential. In this study, using ECR of benzaldehyde to benzyl alcohol as the model reaction for low-temperature stabilization of bio-oil, we have prepared a series of TiO<sub>2</sub>/C hybrid supported catalysts as dual-function materials, wherein, C is used for enhancing the electrical conductivity on the catalyst surface, and TiO<sub>2</sub> is used as a reducible metal oxide, to exploit the lattice oxygen vacancies for facilitating the adsorption of carbonyl oxygen of benzaldehyde to improve hydrogenation rates under mild reaction conditions<sup>1</sup>. 4wt% Pt nanoparticles were supported on all compositions of TiO<sub>2</sub>/C hybrid supports. All catalysts synthesized were thoroughly characterised and evaluated in the ECR of Benzaldehyde, process conditions were optimised and both ECR rates as well as hydrogen evolution reaction (HER) rates were measured.

### Materials and Methods

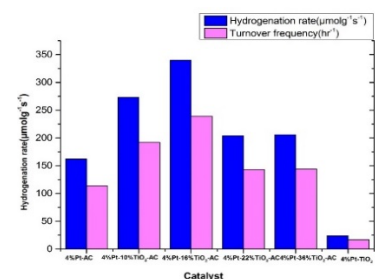
To prepare 3g of the hybrid support with 20%wt TiO<sub>2</sub> loading, the activated charcoal was first dried in vacuum oven for 24 hours, 2.4g of the dried Activated Charcoal was weighed and dissolved in 20ml ethanol and the solution was stirred at 500 rpm for 5 hours. A solution of titanium(iv) isopropoxide in ethanol was prepared, which involved weighing 2.135g of titanium(iv) isopropoxide and dissolving it in 50 ml of ethanol and stirred until a clear homogeneous solution was obtained. The activated charcoal solution and titanium isopropoxide solution were mixed and stirred for 48 hours after which the solution was centrifuge three times to ensure all the unreacted isopropoxide were removed. The residue was then dried for 24 h at 90°C in an oven, and then calcined at 350°C for 4 h to obtain 16%titania loading on TiO<sub>2</sub>/C hybrid support, as measured using ICP-OES analysis. 4 wt% Pt nanoparticles supported on TiO<sub>2</sub>/C catalysts were prepared with incipient wetness impregnation using Pt nitrate solution (assay ~15 %, Johnson-Matthey, UK), as platinum precursor. After impregnation, the materials were dried for 4 h at 120 °C and subsequently calcined at 350 °C for 4 h.

The ECR reactions were carried out in an H-cell with Nafion membrane separating the compartments. The cell consists of two compartments, which served as anodic and cathodic compartment. The working electrode was made up of carbon felt attached to graphite rod, the graphite rod was used to provide the electrical connection to the electrochemical instrument,

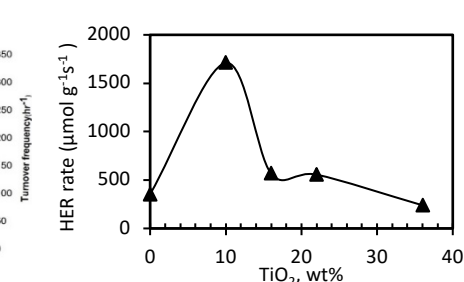
while Platinum coil and Ag/AgCl saturated with 3M KCl served as working and reference electrode respectively. The electrolytic solution used in the experiment was 0.1M sodium acetate-acetic acid buffer solution with pH range between 4.8 to 5.1.

### Results and Discussion

The hybrid support catalyst with 16%TiO<sub>2</sub> loading demonstrated the highest benzaldehyde ECR rate, which could be attributed to the optimal presence of interfacial active sites that benefited from both the conductivity of activated carbon and lattice oxygen vacancies from TiO<sub>2</sub>. These interfacial sites favor the adsorption of carbonyl group of benzaldehyde and thus, facilitates the ECR. The ECR rate increased from 162 to 340 μmolg<sup>-1</sup>s<sup>-1</sup> with increase in TiO<sub>2</sub> loading from 0% to 16% TiO<sub>2</sub> (wt%) loading respectively. Increasing TiO<sub>2</sub> loading beyond 16% resulted in decrease in ECR rate probably due to decreasing in activated carbon which lowers the overall conductivity of the catalyst. The TOF of the hybrid support catalyst with 16 wt% TiO<sub>2</sub> loading is twice that of the 4%Pt-AC catalyst. Besides the ECR, the TiO<sub>2</sub>/C hybrid supports also demonstrated excellent HER rates, with 10 wt% TiO<sub>2</sub>/C as the optimum composition for highest HER rate of 1710 μmolg<sup>-1</sup>s<sup>-1</sup>, due to high current generation on catalyst surface.



**Figure 1.** Benzaldehyde ECR rate on different hybrid support catalysts.



**Figure 2.** Hydrogen evolution reaction (HER) rate at different TiO<sub>2</sub> (wt%) loading.

Reaction conditions: catalyst loading 10 mg, Electrolyte 0.1M Sodium acetate-acetic acid buffer, 20mM Benzaldehyde, Reduction potential -0.6V.

### Significance

All four TiO<sub>2</sub>/C hybrid support catalysts outperformed the individual Pt/TiO<sub>2</sub> and Pt/C supported catalysts, indicating a synergetic effect of combining the carbon and TiO<sub>2</sub> supports. Unlike in thermal hydrogenation, which requires fossil fuel-derived molecular H<sub>2</sub>, ECR technology is more environment friendly, as it generates in situ H<sub>2</sub>, and does not require stringent conditions of high reaction temperature and hydrogen pressure. Pt supported on hybrid TiO<sub>2</sub>/C dual function catalysts are suitable for both ECR as well as HER reactions.

### Reference

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