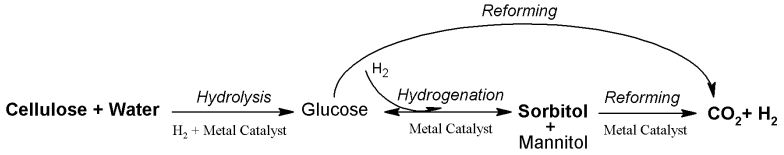
# Conversion of Cellulose to $H_2$ Using Metals Supported Mesorporous Catalysts

Akshat Tanksale, Jorge Norberto Beltramini*, Gao Qing Max Lu
*ARC Centre of Excellence for Functional Nanomaterials, The University of Queensland, St Lucia, QLD 4072, Australia.*
* email: jorgeb@uq.edu.au; phone: +61 7 3346 3803; fax: +61 7 3346 3973

## Introduction

Hydrogen is considered as one of the best alternative clean fuels because of its environment benefits and high efficiency for energy production in fuel cells. Hydrogen can be obtained from carbon neutral resources such as biomass, which is cheap and abundant. Biomass contains water in large proportion and therefore, reforming of biomass in liquid phase is more desirable than steam reforming. After the introduction of aqueous phase reforming of alcohols and ethylene glycol by Dumesic et al. [1,2], our previous studies [3-5] also suggested that hydrogen can be directly produces from aqueous solutions of sugar and sugar alcohols. Our previous results [3-5] were with good agreement with the literature [6,7] which suggested that the activity of the catalyst can be greatly enhanced by using bimetallic catalyst. These metal/alloy catalysts can also be used for hydrolysis / hydrogenation of cellulose to produce sugar monomers or directly sorbitol [8]. Consequently, we demonstrate in this paper that $H_2$ can be produced from cellulose in a two step process, where, cellulose is converted to sorbitol in an aqueous solution in presence of $H_2$ rich gas. Sorbitol can then be reformed in the aqueous phase to produce $H_2$. The overall reaction mechanism is presented in Scheme 1.




**Scheme 1:** Hydrogen production from cellulose in a two step process.

## Experiments and Methods

*Catalyst Preparation*

The mono- and bi-metallic catalysts used in this study were prepared using the wet impregnation. The supports were prepared using sol-gel synthesis. Alumina nano-fibre (Alnf), mesoporous zirconia and mixed oxide of zirconia-ceria-silica of different concentrations were used as supports.

*Characterisation of catalyst*

Surface area of the catalyst was measured using BET technique employing nitrogen physisorption at the temperature of liquid nitrogen in a Quantachrome Autosorb-1C instrument. Pore size distribution was calculated using BJH desorption method. The percentage of metal on support was measured by Inductively-Coupled Plasma Atomic Emission Spectrometer (ICPAES). Temperature programmed reduction (TPR), oxidation (TPO) and CO-desorption (TPD) experiments were conducted using a SRS RGA300 quadrupole mass spectrometer. Full detail of the setup and procedure are published elsewhere [5]. Additional characterisation techniques including XRD, thermogravimetric analysis (TGA), microcalorimetry, TEM and STEM/EDX were also conducted.

*Kinetic Study*

Initial studies of cellulose hydrolysis/hydrogenation were carried out in a Parr batch reactor at 50 bar and 200°C. 2-20% w/w solution of cellulose in water was treated with Pt, Ni and Ni-Pt catalysts supported on high surface area alumina nanofibre (Alnf), zirconia ($ZrO_2$) and ceria-zirconia-silica (CZS) supports. The catalysts were then used in a fixed bed reactor for conversion of 10% w/w solution of sorbitol in water. Gas samples were analysed at 1hour interval in a Shimadzu GC17A gas chromatographer using a packed column. Sorbitol solution were analysed in an HPLC from external source. The details of the fixed bed reactor setup and catalyst preparation and pre-treatment methods are described elsewhere [5].

## Results and Discussion

The results of TPR showed that Ni catalyst supported on alumina nanofibre (Alnf) exhibits two peaks of reduction at 700°C and 800°C. With the addition of Pt and Pd there is a significant decrease in reduction peak by 250°C and 150°C, respectively. This is remarkable because the atomic ratio of Ni to Pt and Pd in the catalyst is 33:1 and 18:1, respectively. Aqueous phase reforming reaction studies carried out in the fixed bed reactor on mono-metallic and bi-metallic catalysts supported on alumina nanofibre suggests that addition of Pt and Pd as promoters to Ni increases its activity to more than 3–6 times that of Ni/Alnf. The rate of $H_2$ formation increased from 1.5µmol/min.gmCat for Ni/Alnf to over 7µmol/min.gmCat for Ni-Pt/Alnf.

## Conclusions

The results provided the evidence that both Pt and Ni are present in nano-sized rod shaped particles. The kinetic study conducted on fixed bed reactor showed that the bi-metallic catalysts exhibit substantially greater activity than the corresponding pure metal catalysts. Higher $H_2$ selectivity was also obtained at high sorbitol conversion. It is believed that the alloying effect of these systems leads to lowering of the CO heat of adsorption.

## Significance

The research carried out in this project was partly applied and partly fundamental study of the nature of catalysts for $H_2$ production from biomass resources for the fuel cell application.

## References

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