# Cellulose Aqueous Phase Reforming (APR) using Ni and PtNi based catalyst for hydrogen generation: the unexpected effect of reductive atmosphere

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## Significance and Relevance

This study demonstrates the effectiveness of layered double hydroxide (LDH)-derived catalysts in producing hydrogen from waste cellulose via aqueous phase reforming (APR) with a one-pot approach that minimizes humin formation, enhancing hydrogen yields supporting the development of sustainable energy solutions, contributing to the hydrogen economy and promoting the utilization of wastes for energy generation.

*Preferred and 2nd choice for the topic: H2 storage and transportation, Green hydrogen production, energy vectors*
*Preferred presentation*: Oral preferred or Short Oral

## Introduction and Motivations

As part of the hydrogen economy, various processes for producing hydrogen from renewable sources are being explored. One promising method involves the catalytic conversion of waste biomass, particularly cellulose, into hydrogen. Typically, cellulose is converted by hydrolysis to produce an aqueous glucose solution, which can then be subjected to aqueous phase reforming (APR) to yield hydrogen. This catalytic process resembles methane steam reforming and generates hydrogen and carbon monoxide from carbon-based substrates[1,2]. Unlike methane, glucose contains complex structures with C-C and C-O bonds alongside C-H bonds, which facilitates its decomposition and lowers the temperature required for the endothermic reforming reaction (200-250°C). Consequently, APR can be conducted at autogenous pressure within the liquid phase.

$$C_6H_{12}O_6 \rightleftarrows 6CO + 6H_2 \qquad \text{Glucose APR}$$

The low-temperature operation enables simultaneous execution of the reforming reaction and the water gas shift (WGS) reaction, which consumes CO produced during reforming and enhances hydrogen yield. However, when glucose is heated above 150°C, it tends to decompose into solid humins[3], which obstructs hydrogen production and blocks catalyst active sites. In this study, we employed a one-pot approach by directly using a cellulose aqueous mixture in APR with a suitable catalyst that possesses both acid-base and redox properties. This method allows for controlled hydrolysis of cellulose, yielding low glucose concentrations that are quickly consumed in the reforming process, thereby preventing humin formation. Tailored catalysts are essential for this approach

## Materials and Methods

The LDH-based catalysts were synthesized via coprecipitation and subsequently calcined to form mixed oxides. The final catalysts consisted of $Ni^0$ supported on MgAl mixed oxide obtained through reduction under $H_2$. Characterization of the catalysts was performed using XRD, nitrogen physisorption, TEM, TPD, and TPR/OR analyses. An autoclave was charged with cellulose (1.5g), catalyst (0.4g), and water (50.0g) under $N_2$ or $H_2$ atmosphere and heated to 250°C. Gas and liquid products were analyzed via GC and HPLC respectively.

## Results and Discussion

The $Ni^0/Mg(Al)O$ catalysts exhibited both redox and acid-base functionalities necessary for catalyzing hydrolysis and reforming reactions as well as retro-aldol reactions. In glucose APR experiments, minimal hydrogen production was observed due to humin formation; however, a significant hydrogen yield (>20%) was achieved using cellulose. This demonstrates the benefits of a one-pot process that integrates hydrolysis with APR. The effect of Ni content on hydrogen yield was also assessed; initially increasing Ni content enhanced yield but resulted in decreased yield at higher concentrations due to larger Ni particle formation reducing the overall metallic surface area. The study also focused on identifying liquid products and their corresponding reaction pathways—an area often overlooked in existing literature. Notably, glucose was not detected in the liquid phase, indicating its rapid consumption by APR compared to its generation from cellulose hydrolysis. Among the identified products were lactic acid, acetic acid, and ethylene glycol; the latter likely serves as an intermediate for hydrogen production due to its ease of reforming. Adding Pt to the NiMgAl catalyst facilitated a reduction in the temperature required for reduction (as indicated by TPR), thereby enhancing both the reforming reactions and C-C bond cleavage, which increased the hydrogen yield to 40%. The highest yield, exceeding 50%, was achieved in a hydrogen atmosphere, which accelerated the hydrolysis rate and promoted rapid reforming due to the NiPt active phase. The influence of reaction time was investigated to propose a reaction mechanism, while varying reduction temperatures helped identify the optimal reduction procedure. Additionally, Pt was impregnated onto a commercial support, demonstrating the superior performance of the catalyst developed in this study and the reaction mechanism was drawn starting from the obtained results.

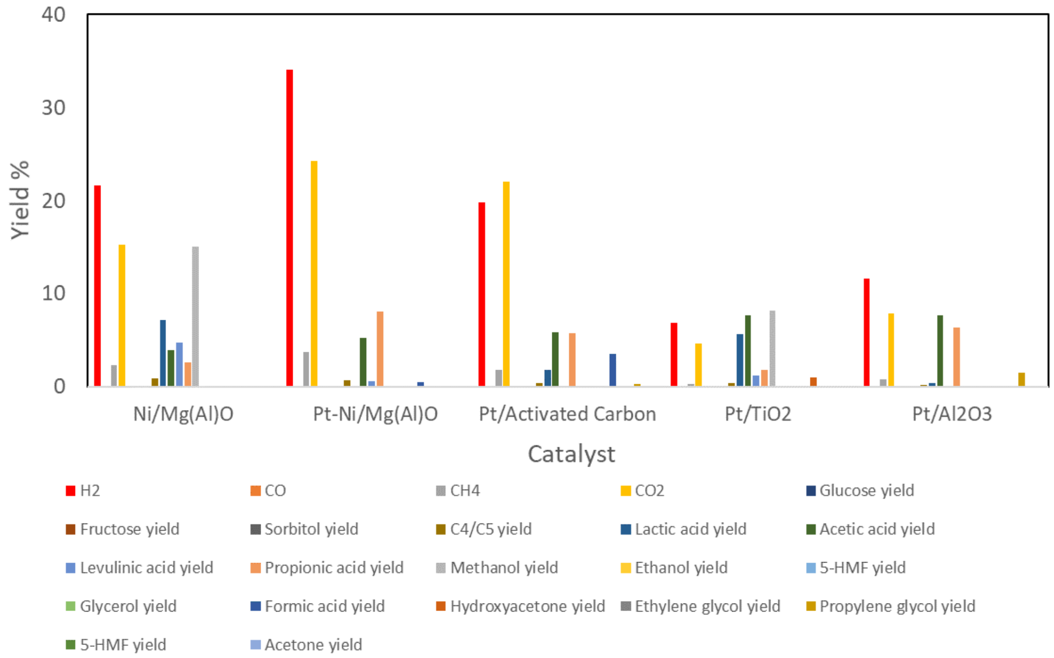

**Figure 1. Gas and liquid phase products obtained over different Pt-based catalyst at 250°C for 3 h.**

## References

1. A. Fasolini et al., *Catalysts* **2019,** *9.9, 722*.
2. A. Fasolini et al., *Catalysts* **2019,** *9.11, 917*
3. S. Taghavi et al. *Catalysts* **2020,** *8.7, 843*