# Catalytic Conversion of Carbohydrates into 5-HMF on Reduced Graphene Oxide Supported Metal Catalysts

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**Abstract:** Reduced graphene oxide/metal supported catalysts (rGO-M) were synthesized by employing a fast and eco-friendly microwave-assisted process, which facilitated the simultaneous reduction of graphene oxide and formation of metal nanocrystals. This system was tested for potential use as catalyst material through the catalytic conversion of glucose into 5-HMF.

**Keywords:** Reduced graphene oxide, metal supported catalyst, 5-HMF

## 1. Introduction

Cellulosic biomass provides renewable alternatives to fossil-fuel resources for the sustainable production of liquid fuels and valuable chemicals. The challenge for the effective utilization of these sustainable resources is to develop cost-effective processing methods for the transformation of carbohydrates into value-added chemicals. Carbohydrates, predominantly cellulose, represent the largest fraction of biomass, and various strategies for their efficient use as a commercial chemical feedstock are currently being established with the aim to supplement and ultimately replace fossil fuels. To achieve this goal, it is pivotal to develop more efficient and environmental-friendly methods to convert cellulose into useful chemicals. In particular, catalytic conversion of biomass-derived carbohydrates to 5-hydroxymethylfurfural (HMF) opens the possibility of a wide variety of products that could serve as solvents, polymers or fuels (1).

In this study, we focused on the use of graphene oxide (GO) as catalyst support. GO, a single sheet of graphite, is an especially promising form of nanoscale carbon with a rare combination of extremely high specific surface area, exceptional thermal/electrical conductivity, and good chemical and thermal stability. Current mass-scale production of graphene is based on chemical exfoliation of graphite in strong acids. The oxidation procedure introduces oxygen atoms to the basal planes and edges of graphene layers in the form of functional groups, such as hydroxyl, epoxide, keto, and carboxyl. The utilization of graphene as a two-dimensional support to anchor catalyst nanoparticles (NPs) and facilitate electron transport opens up new possibilities for designing the next generation catalysts (2). In addition, the oxygen functional group on the GO surface can be deoxygenated by heat, light or in contact with hydrazine, and it becomes a reduced type graphene oxide (rGO), with many defect structure and high electron conductivity. Here, we demonstrate the effectiveness of a rGO/metal oxide nanoparticle hybrid catalyst in transforming carbohydrates to HMF starting with glucose as a model compound.

## 2. Experimental

GO was synthesized by ultrasonic exfoliation of graphite oxide obtained by Hummers method (3) in aqueous solution. rGO-M was produced by mixing the synthesized GO with the metal M (Ni, Co, Pt, Fe) and then reducing the obtained GO-M with hydrazine. Afterwards, the obtained rGO-M was placed in a reaction vessel together with a water solution of glucose into a microwave oven where HMF was generated. The reaction products were analyzed by the use of a HPLC system and rGO-M catalysts were characterized by the use of SEM, PXRD, XPS.

## 3. Results and discussion

HMF synthesis reaction was carried out on a biphasic system (water/THF) using each synthesized rGO-M as a catalyst. From the results it was found that the best HMF yield can be obtained when rGO-Ni catalyst is used (Figure 1). Therefore, the target was narrowed down to rGO-Ni catalyst, for what SEM, PXRD, XPS measurement and determination of catalyst optimum condition were carried out. As a result of SEM and PXRD measurement, it was found that the rGO-Ni catalyst had Ni aggregates of about 100 nm to 200 nm on rGO in the form of oxide and hydroxide as can be seen in Figure 2. In addition, pH and reaction time dependent HMF yields were study to determine to the optimal HMF synthesis reaction conditions of the rGO-Ni catalyst. It was found that, pH 4 yielded the best HMF yield, whereas as time of reaction progressed, HMF yield was found increasing proportionally until 40 minutes and then becomes constant. However, since the conversion of glucose continue to increase after 40 minutes, it was found that HMF was hydrolyzed into humins compounds by microwave reaction conditions. Therefore, in order to prevent decomposition of HMF, the experiment was carried out with two phase solvents using THF as the extracted organic phase. As a result, HMF yield greatly improve. Figure 3 shows that when no catalyst was used, HMF yield was 42 % and when rGO-Ni was used, HMF yield was increased to 75 %. This results shows that we successfully succeeded in suppressing the decomposition of HMF and obtaining HMF with higher yield by conducting the reaction solvent into two phase systems of THF and water.

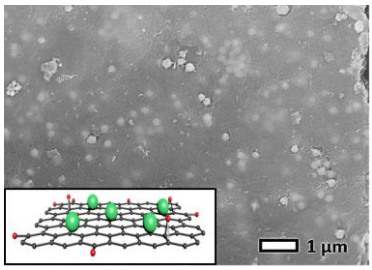


**Figure 2.** Hybrid of rGO and Ni nanoparticles

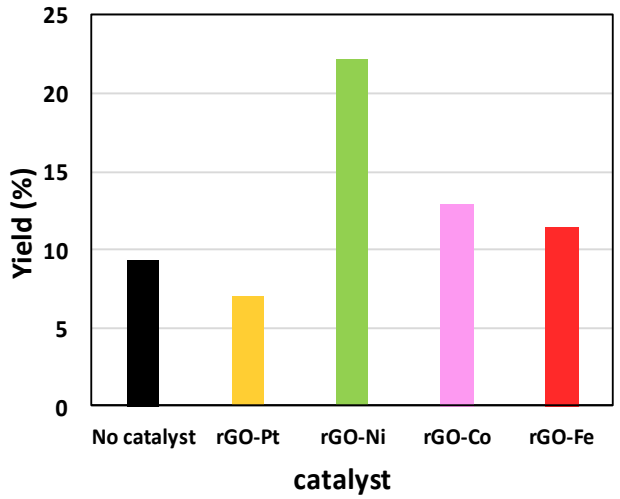


**Figure 1.** HMF yield using rGO-M as catalyst.

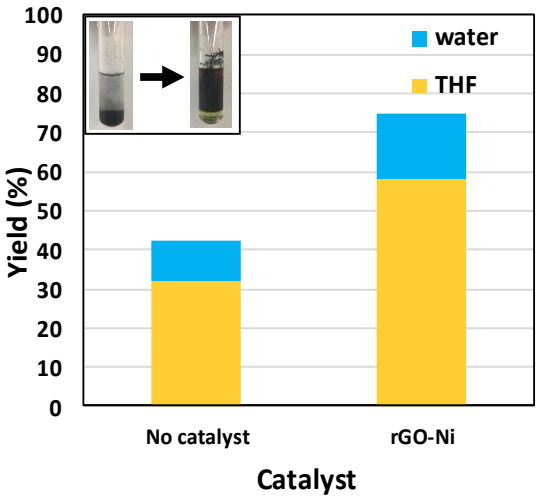


**Figure 3.** HMF yield in two phase reaction solvent.

## 4. Conclusions

We demonstrated that rGO-metal hybrids are an effective catalyst for the production of HMF from glucose. Especially, rGO-Ni hybrids of hydrazine reduction indicated the best catalytic activity. In addition, rGO-Ni hybrids of hydrazine suggested that Ni agglomerates exist on rGO and that Ni exists also in the form of oxide and hydroxide. Furthermore, we succeeded in improving the HMF yield up to 75 % by conducting the reaction using a catalyst of rGO-Ni in two phase systems of water and THF.

## References

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