Ni-DOPED TUNGSTEN CARBIDE CATALYSTS FOR THE SELECTIVE PRODUCTION OF ETHYLENE GLYCOL FROM CELLULOSIC MATERIALS

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Significance and Relevance

The selective conversion of glucose and cellulose toward ethylene glycol formation, was successfully obtained over Ni-doped tungsten carbide catalysts supported on different carbon materials. The role of nickel and the support were established. The high yield and selectivity of EG obtained directly from cellulose and the cheapness of the catalyst, pave the way to a possible use of this materials for the conversion of more complex matrices such as paper industry waste (PPMS), with the possibility to obtain high-value added ethylene glycol in a new renewable way.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion / Circular economy
Preferred presentation: Oral preferred or short oral

Introduction and Motivations

The utilization of waste and biomass for material production presents a promising pathway, particularly regarding environmental sustainability compared to methods based on fossil resources.[1] Cellulose and cellulosic waste, such as pulp and paper mill sludge (PPMS), hold significant appeal due their abundance and non-competition with food production. Transforming these materials into valued products, like polyols, offers a fresh, sustainable source of materials, especially for commodity polymers production.[2] Traditionally, noble metal catalysts like Pt, Pd, and Ru were employed for cellulose valorization through hydrogenation reactions, but there is a strong push towards utilizing more readily available non-noble metals. Hence, we propose catalytic systems based on tungsten carbides supported on different carbon supports, combined with Ni, for the in situ hydrolysis of cellulosic waste into glucose, and subsequent selective hydrogenation to ethylene glycol.

Results and Discussion

Different Ni doped tungsten carbide catalysts were prepared and tested under different conditions in glucose or cellulose hydrogenation with the aim of optimizing ethylene glycol production. As the support we selected three different carbons, namely an activated carbon (X40S), a carbon black (Vulcan XC72) and graphene nano-platelets (GNP). The catalysts were prepared by incipient wetness impregnation and then calcined in H_2.

The catalysts were selected on the basis of their influence in balancing the different possible reaction pathways (isomerization, retroaldol, hydrogenation, degradation). The nickel presence resulted fundamental not only for the hydrogenation reaction but also for WC_2 formation, essential for promoting retroaldol reaction, i.e. first step for EG formation (Fig 1).

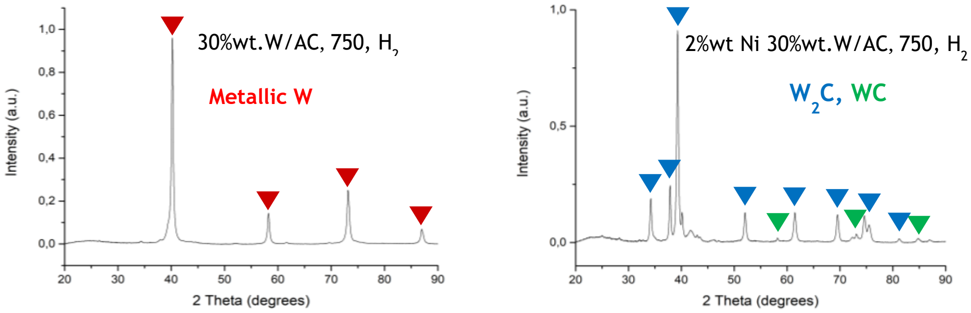

Fig 1-*XRD spectra of catalysts prepared in absence or presence of Ni, after the same calcination conditions (750°C, H_2)*

All the materials were characterized by multiple techniques such as XRD, FESEM, BET, XPS EDS. Regarding the catalytic activity, the materials in which the nickel was not present, led to the formation of undesired degradation products. The catalytic optimized conditions, for both glucose and cellulose, were found varying temperature, hydrogen pressure and reaction time. Starting from glucose a 35% yield of EG has been obtained with the catalyst supported on activate carbon (X40S) at **220°C** under **40 bar** of hydrogen for **30 minutes**. For the direct conversion of cellulose, as expected, we have to use harsher conditions due to the initial de-polymerization step, but an outstanding **51%wt** yield of EG has been obtained at **245°C** under **60 bar** of hydrogen for **2.5h**. We found that in this latter case the best catalytic performances have been obtained using the graphene nanoplates (GNP) as the support (Fig.2). We correlate this surprising result to the low local concentration of glucose deriving from the depolimerisation of cellulose thus a possible match between the kinetic of de-polymerization and the following retro-aldol condensation/hydrogenation step limiting the formation of by-products.

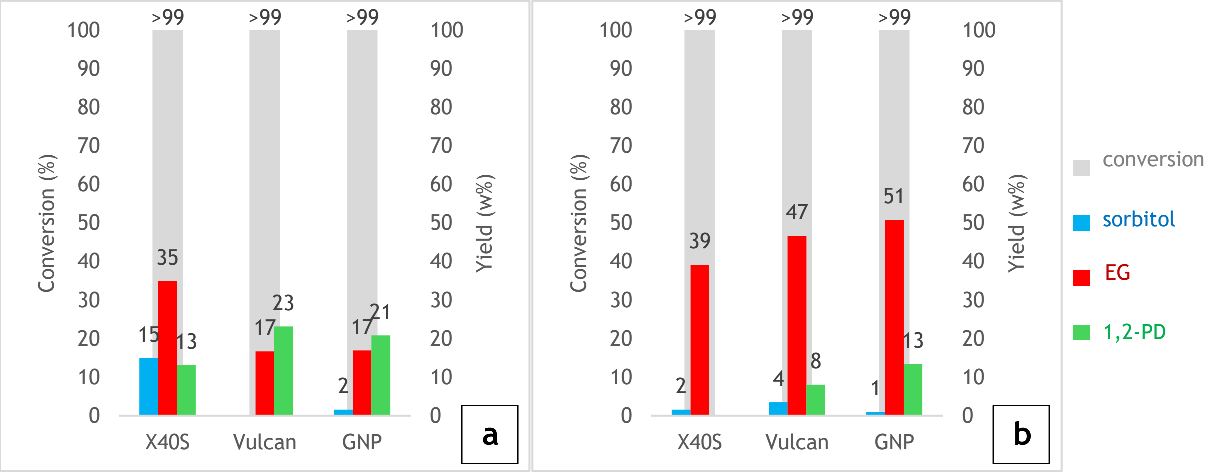

Figure 2-*Catalytic performances of the different supported catalysts on Glucose (**a**) and Cellulose (**b**)*

FESEM analysis on the spent catalysts showed in both cases (glucose and cellulose reactant) the formation of tungsten oxide WO_3, which might be derived by a partial dissolution and oxidation of the WC_2 in the reaction media. For this reason, the nature of the true active species is still to be assessed and further analysis will be performed to shed light on the role of the support.

References

1. Atsushi Fukuoka, Paresh L. Dhepe, *Angew. Chem. Int. Ed.*, **2006**, 45, 5161-5163
2. Mee Kee Wong, Serene Sow Mun Lock, Yi Herng Chan, *Chem. Eng. J.*, **2023**, 468,143699.

Acknowledgement

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