Supported ruthenium as an efficient catalyst for the valorization of platform molecules derived from biomass

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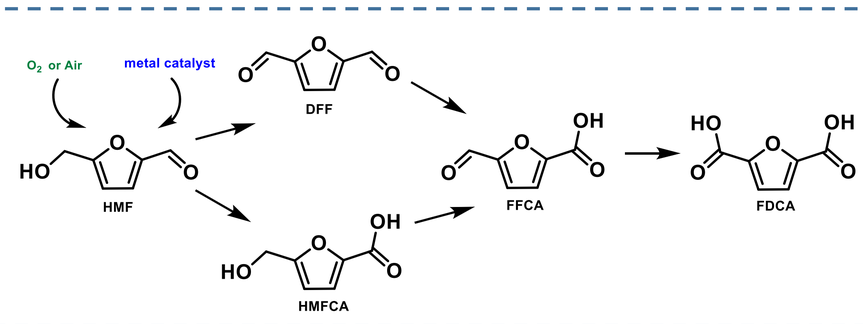
INTRODUCTION

5-hydroxymethylfurfural (HMF) is a highly versatile platform molecule derived from the dehydration of hexoses (glucose or fructose) that can be converted into high value-added chemical compounds through different catalytic pathways. Diformylfuran (DFF) derived from the oxidation of HMF is of great interest, due to its use as a precursor for numerous applications in the fine chemical industry such as pharmaceuticals, agrochemicals and polymers. However, the selective oxidation of the hydroxymethyl group of HMF, to obtain DFF is not a simple process, since in many cases the over-oxidation of the oxygenated groups occur, decreasing the selectivity to DFF.
In this work we have designed a Ru/C catalyst for HMF oxidation that allow to obtain high yields and selectivity to DFF under mild reaction conditions using O_2 as oxidant.



The use of catalysts based on Ru nanoparticles allows to obtain high yields and selectivity of DFF.

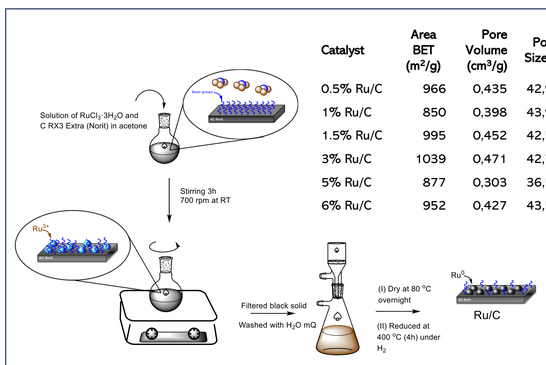
RESULTS

The reaction was performed using Ru nanoparticles supported on different supports, such as Al_2O_3, Carbon, and Al-Mg mixed oxide. The Ru/C catalyst exhibited the highest activity and selectivity to DFF. Reaction conditions, and solvent were optimized, and trifluorotoluene (TFT) was established as the best solvent.
Optimization of Ru nanoparticle size was performed by synthesizing a series of catalysts with different Ru loading.
It was showed that there is an optimum Ru cristal size that exhibits the maximum catalytic activity.

Catalyst	Conv. HMF (%)	Yield DFF (%)	Yield FFCA(%)	Yield HMFCA (%)	Yield FDCA (%)	Select. DFF (%)	TOF (h^{-1})[c]	TON[d]
0.5% Ru/C	81	81	-	-	-	100	114	67
1% Ru/C [a]	94	93	-	1	-	99	58	79
1.5% Ru/C	82	82	-	-	-	100	58	75
3% Ru/C	99	99	-	-	-	100	157	80
5% Ru/C [b]	94	92	-	2	-	98	85	77
6% Ru/C	88	88	-	-	-	100	62	73
C [e]	25	25	-	-	-	100	-	-

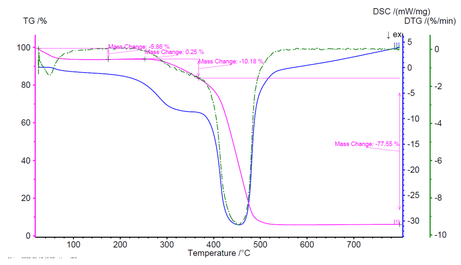
Reaction conditions: HMF (0.5mmol), HMF/Ru ratio = 84, 120 °C, 6 bar O_2
[a] Commercial catalyst from Johnson Matthey.
[b] Commercial catalyst from Sigma-Aldrich
[c] TOF are calculated as initial reaction rate of disappearance of HMF divided by Ru (mmol/g).
[d] TON are calculated as maximum mmol of DFF divided by Ru (mmol).
[e] 20 mg of C was used.

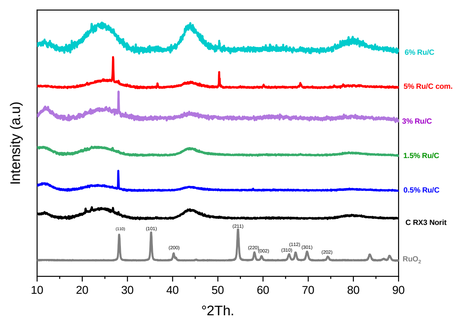
CHARACTERIZATION AND SYNTHESIS OF CATALYST

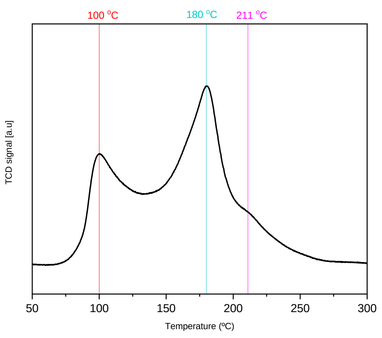


Catalyst	Area BET (m^2/g)	Pore Volume (cm^3/g)	Pore Size (A)	% Ru
0.5% Ru/C	966	0,435	42,989	0,84
1% Ru/C	850	0,398	43,932	1,07
1.5% Ru/C	995	0,452	42,582	1,58
3% Ru/C	1039	0,471	42,747	3,1
5% Ru/C	877	0,303	36,556	4,5
6% Ru/C	952	0,427	43,514	5,5

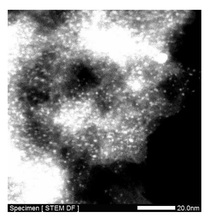
The different catalysts (0.5, 1.5, 3, 5, 6% Ru/C) were prepared through the deposition-precipitation method, mixing the appropriate amount of Carbon with a solution of ruthenium chloride in acetone. Then, it was reduced with a stream of H_2.
Results indicate that during the inmovilization process most of Ru is deposited in Carbon. 3% Ru/C contains 3.1% of Ru (ICP measurement).

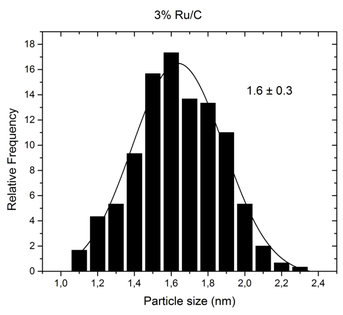


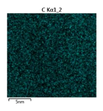




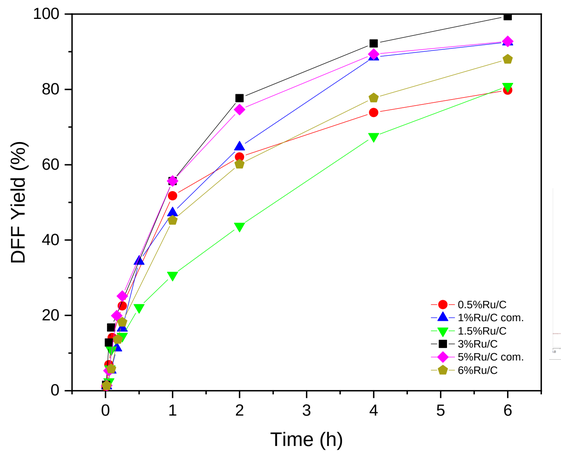
The size of metallic nanoparticles was measured using TEM (transmission electron microscopy).

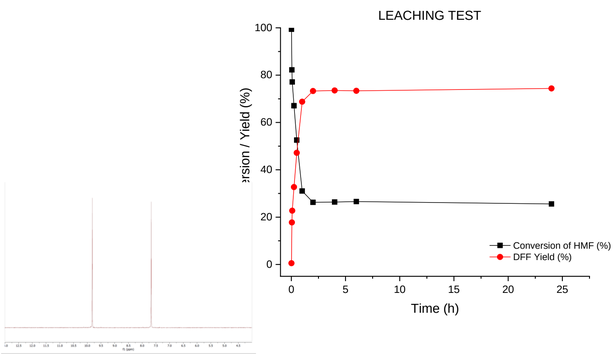






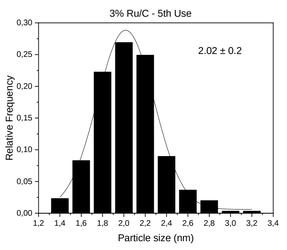
TPR analysis shows peaks bellow 200 °C are related to the reduction of $RuCl_3$, and reduction of the metal precursor to metallic state. Peaks above 200 °C corresponds to a reduction of ruthenium oxide RuO_x

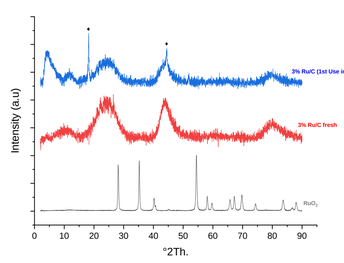


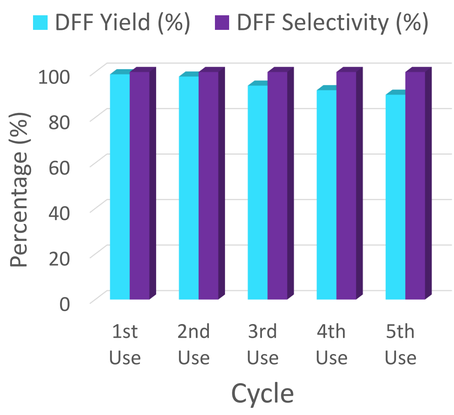


^{1}H NMR of reaction with 3%Ru/C clearly shows that the majority is DFF

The reusability of the Ru / C catalyst was studied. After the reaction, the catalyst was separated from the reaction media by filtration, washed with acetone in a soxhlet system, and then activated with H2 and reused in the next cycle. Ru/C catalyst can be reused at least 5 consecutive times without significant loss of activity.







CONCLUSION

- *2,5-diformylfuran (DFF) was selectively obtained from the selective oxidation of 5-hydroxymethylfurfural (HMF) using a carbon-supported ruthenium catalyst (Ru/C) with molecular oxygen under mild reaction conditions.*
- *Ru/C is an effective and recyclable catalyst for the aerobic oxidation of HMF to DFF, affording DFF in ~99% yield in TFT.*
- *3% Ru/C with a nanoparticle size of 1.6 nm resulted the most active catalyst.*

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ACKNOWLEDGMENTS

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