

Supplementary Information for
Gas-phase cascade upgrading of furfural to 2-methylfuran using methanol as
H-transfer reactant and MgO based catalysts.

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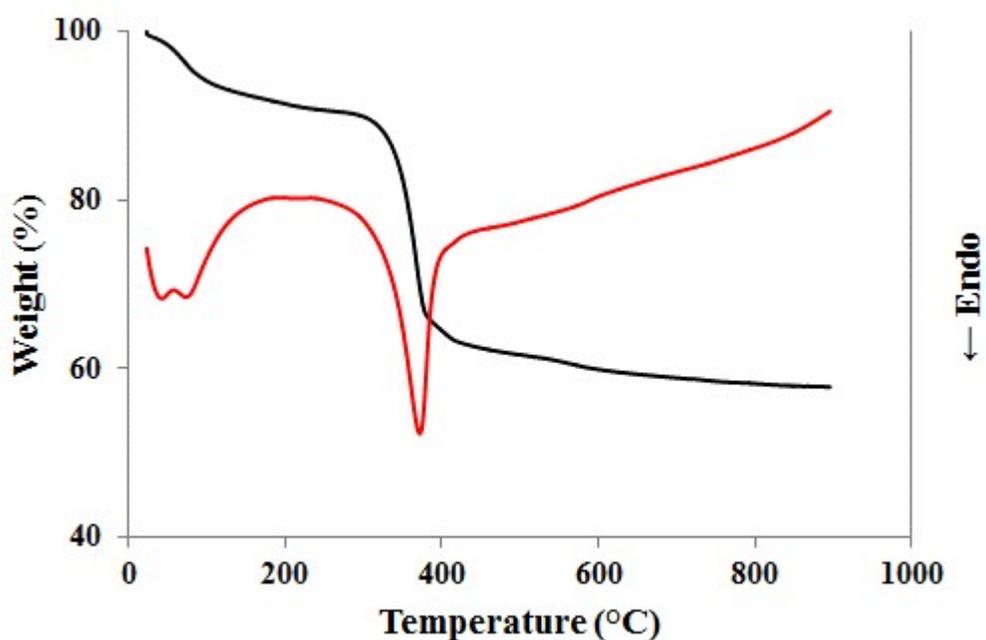


Figure S1 – Thermogravimetric (—) and differential thermal (—) analyses (TGA/DTA) of MgO precursor in air.

The thermal decomposition of $\text{Mg}(\text{OH})_2$ showed two major mass loss at 60-100 and 360-380°C, equal to 5 and 30%, respectively. The first step can be attributed to the loss of adsorbed water, while the brucite-layer dehydroxylation occurred between 250 and 400°C.

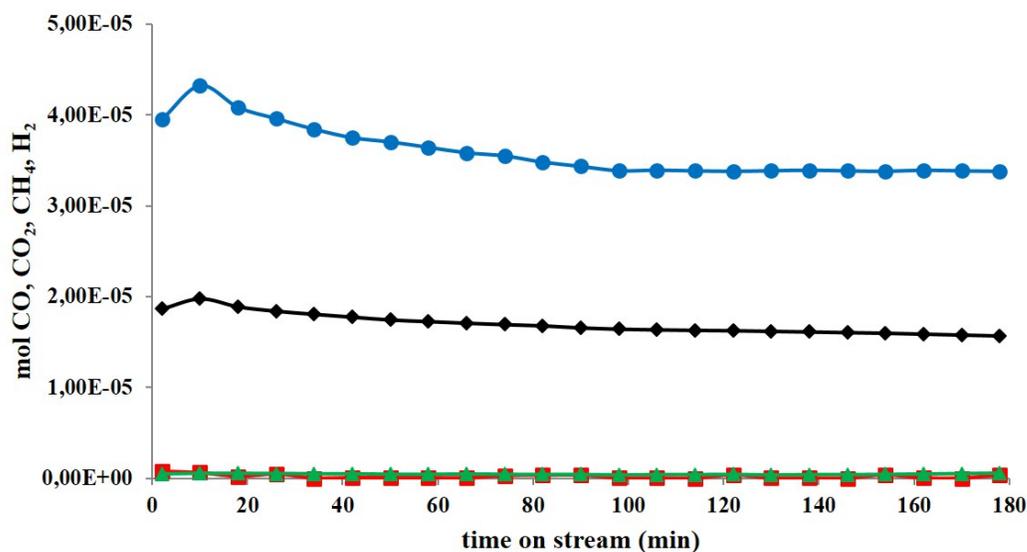


Figure S2-A. Number of moles of gaseous products formed, based on time, during the decomposition of methanol over MgO. Feed composition: CH₃OH 50% , N₂ 50%; pressure 1 atm, temperature 380°C, overall gas residence time 1,1 s. Symbols: ♦ CO, ■ CO₂, ▲ CH₄, ● H₂.

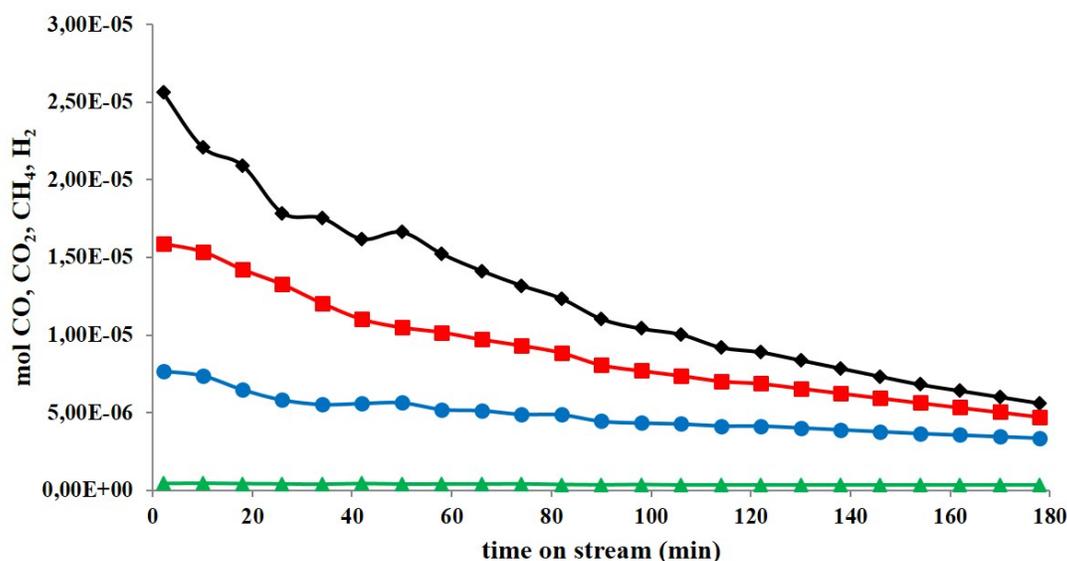


Figure S2-B. Number of moles of gaseous products formed, based on time, in the reaction of FU reduction with methanol over MgO. Feed composition (mol %): FU 5%, CH₃OH 50% , N₂ 45%; pressure 1 atm, temperature 380°C, overall gas residence time 1,1 s. Symbols: ♦ CO, ■ CO₂, ▲ CH₄, ● H₂.

Table S1 Effect of total volumetric flow and catalyst particle size on the conversion of FU with MgO catalyst. Feed composition (mol %): FU 5%, CH₃OH 50%, N₂ 45% ; Pressure 1 atm, overall gas residence time 0,5 s.

Test	Volumetric flow (ml/min)	Catalyst particle size (μm)	Temperature (°C)	FU Conversion (%)
1	60	250÷595	320	33
2	120	250÷595	320	32
3	60	250÷595	250	34
4	60	250÷400	250	37
5	60	125÷177	250	35
6	60	250÷595	350	35
7	60	250÷400	350	41
8	60	125÷177	350	36
9	60	250÷595	400	41
10	60	250÷400	400	45
11	60	125÷177	400	40

For the purpose of the study, it is important to ensure that the rate data are obtained under kinetically controlled regime. Therefore, preliminary experiments were conducted to investigate the influence of both the total volumetric flow and the catalyst particle size. As shown in Table S1, both the external and the internal diffusion as limiting steps can be ruled out, because the conversions of FU showed minimal variations when either the total volumetric flow was varied or catalysts with different particle size were used, while keeping the same overall gas contact time in all experiments.

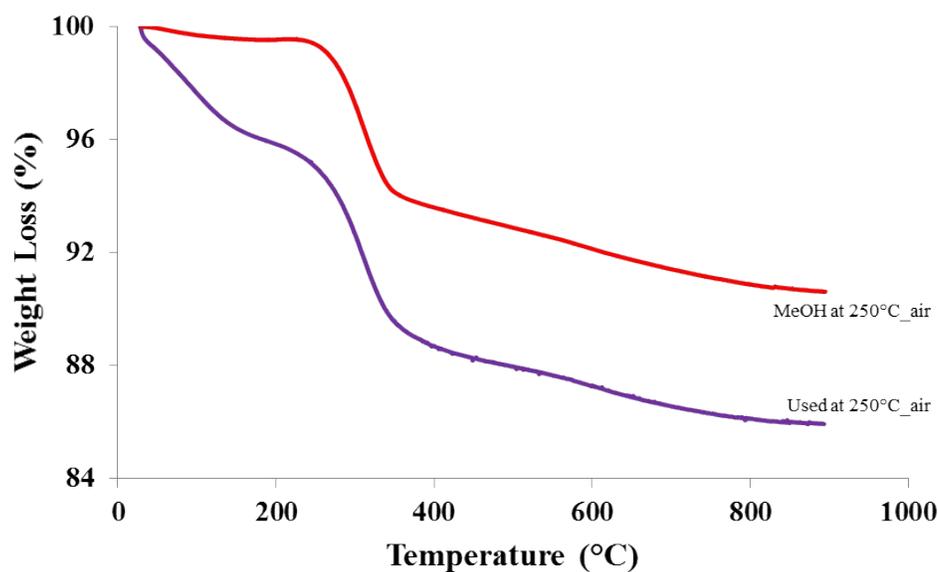


Figure S3 – Comparison between TG profiles of MgO used in FU reaction with methanol at 250°C (—), and treated under the same reaction conditions but without FU (i.e., with methanol only) (—).

Table S2. Effect of the reducing agent on the activity of MgO. Feed composition (mol %): FU or FAL 5%, CH₃OH or H₂ 50%, N₂ 45%, temperature 250°C, pressure 1 atm, overall gas residence time 1.1 s.

Reagents	Conversion, Selectivity (%)				
	FU	FAL	MFU	CPS	C-Loss
FU + CH ₃ OH	54	95	0	0	5
FU	0	0	0	0	0
FU + H ₂	0	0	0	0	0
FAL + H ₂	100	5	0	0	0

Results demonstrate that MgO is able to reduce FU to FAL in presence of methanol, while either without methanol or using H₂ the reaction did not occur at all. Similar results were obtained feeding FAL; however, in this latter case, also FU formed (5% yield). These tests confirm the stability of FU and FAL over MgO, and also allowed to attribute the weight loss shown in the TG profile (Figures 4 and S3) to some carbonaceous species derived from methanol.

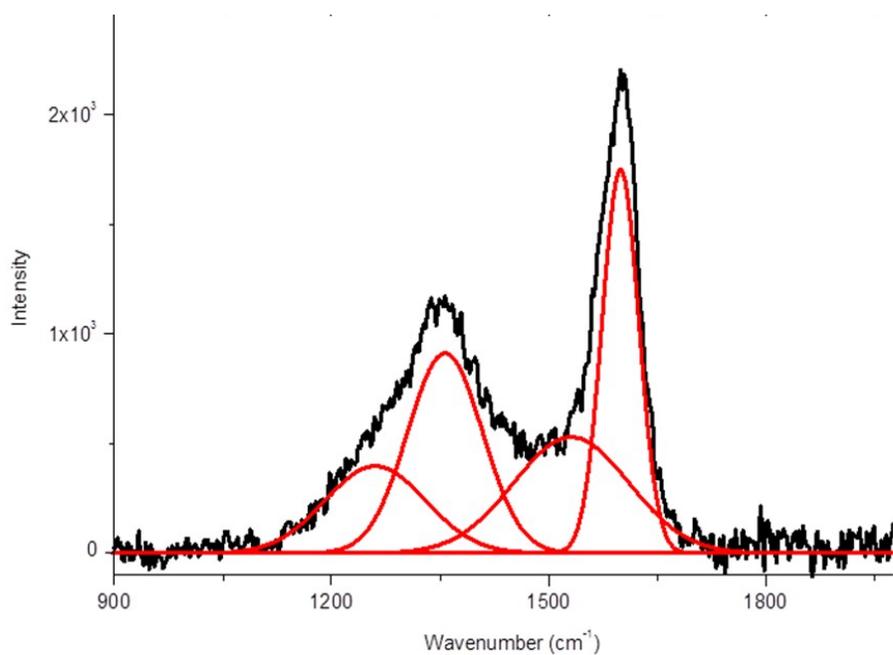


Figure S4 - Raman spectrum of MgO used at 500°C showed the presence of bands attributable to coke.

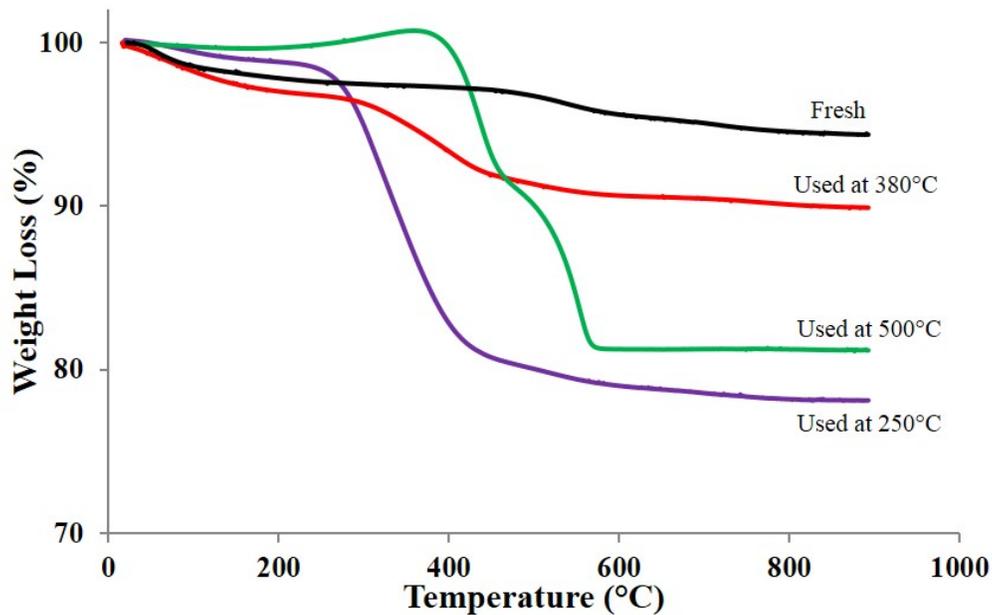


Figure S5. Thermogravimetric analysis (TGA) in air: fresh Mg/Fe/O calcined at 500°C (—); spent Mg/Fe/O used in catalytic test at 250°C (—), at 380°C (—) and at 500°C (—).

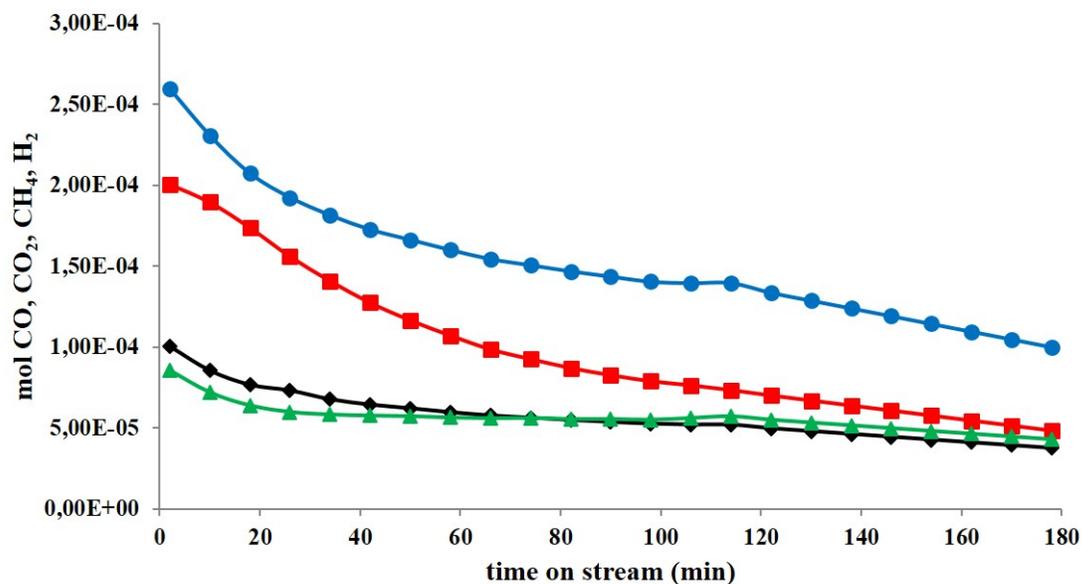


Figure S6 – Mg/Fe/O catalyst. Number of moles of gas formed, based on the time, in the reaction of FU reduction with methanol. Feed composition (mol %): FU 5%, CH₃OH 50% , N₂ 45%; pressure 1 atm, temperature 380°C, overall gas residence time 1,1 s. Symbols: ◆ CO, ■ CO₂, ▲ CH₄, ● H₂.

Table S3 Effect of the reducing agent on the activity of Mg/Fe/O. Feed composition (mol %): FU or FAL 5%, CH₃OH or H₂ 50%, rest N₂; temperature 380°C, pressure 1 atm, overall gas residence time 1.1 s.

Reagents	Conversion, Selectivity (%)				
	FU	FAL	MF	CPs	C-Loss
FU + CH ₃ OH	93	1	79	2	18
FU	20	0	0	0	100
FU + H ₂	20	0	25	0	75
FAL + H ₂	5	100	42	0	53

Results shown in Table S3 indicate that Mg/Fe/O is able to activate H₂ and hydrogenate FU to MF, but with low MF selectivity (25%); in this case the conversion of FU was 20% only (with methanol it was 93%), and a 75% C-loss was detected, evidencing the considerable extent of FU degradation to carbonaceous residua. Nevertheless, with Mg/Fe/O some influence on FU reduction with methanol due to the *in-situ* produced H₂ cannot be excluded.

Total FAL conversion, with 42% selectivity to MF, and 53% C-loss were registered in the reaction of FAL with H₂.

Table S4. Effect of the catalyst type on performance. Feed composition (mol %): FU 5%, CH₃OH 50%, rest N₂; temperature 380°C, pressure 1 atm, overall gas residence time 1.1 s. All samples were calcined at 500°C for 6 h.

Catalyst	Mg/Fe atomic ratio	Conversion, Selectivity (%)			
		FU	FAL	MF	C-Loss
MgO	-	54	75	5	20
Mg/Fe/O Coprecipitated	2:1	93	1	79	20
Mg/Fe/O Coprecipitated	10:1	68	17	52	31
Fe ₂ O ₃	-	73	2	10	88
Fe ₂ O ₃ /MgO Mechan. Mixed	10:1	80	25	52	23