Supplementary Information

Exploiting H-transfer as a tool for the catalytic reduction of bio-based building blocks: the gas-phase production of 2-methylfurfural using $FeVO_4$ catalyst

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Figure S1 - XRD patterns of the dried (black) and calcined (red) $FeVO_4$. Reference patterns: (●) Fe_2O_3, (▬) $FeVO_4$.

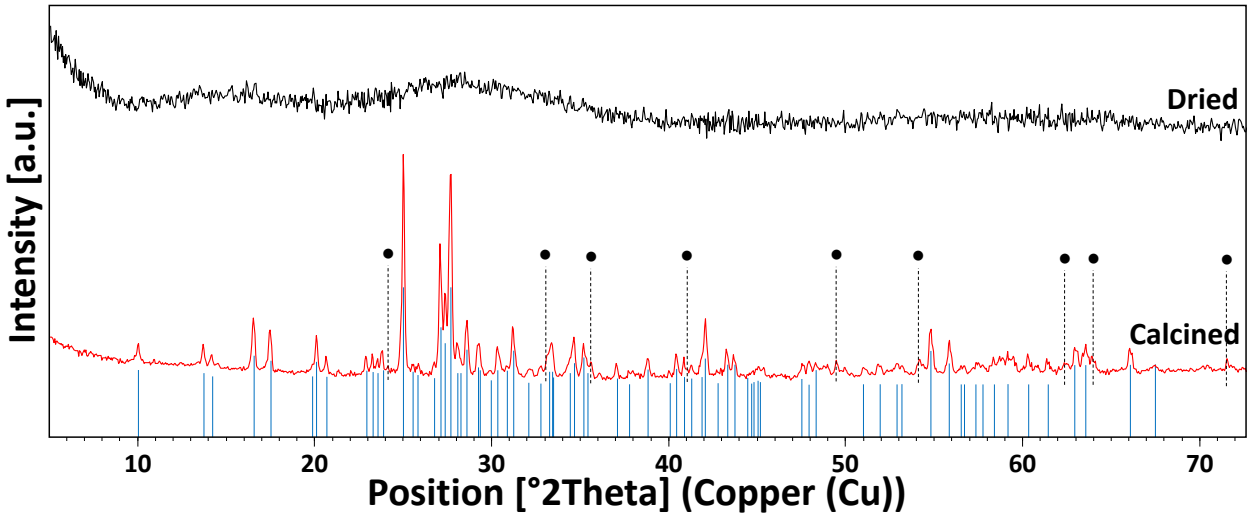
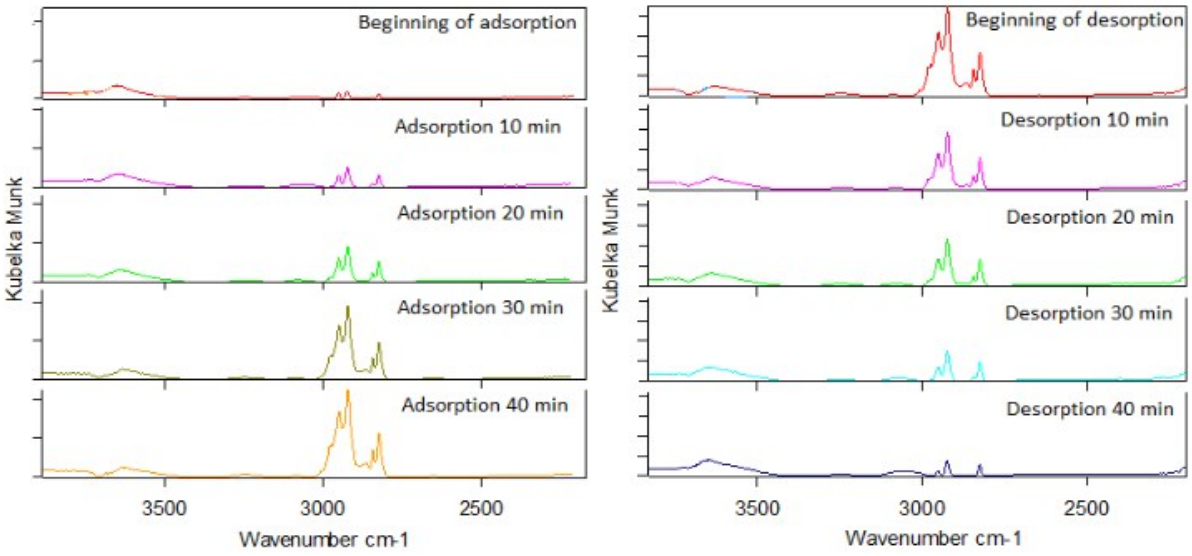


Figure S2 – DRIFT spectra recorded after methanol adsorption (left side) and desorption (right side) over $FeVO_4$ catalyst performed at 85°C. All the reported spectra have the same Y-axis scale



DRIFT spectra recorded after methanol adsorption and desorption; these experiments allow to demonstrate that methanol adsorbs in two different ways over the catalyst surface. The most important one is a dissociative adsorption that brings to the formation of methoxy species according to the IR bands observed at 2930 and 2828 cm^{-1}. On the other hand, methanol could be also adsorbed in an undissociative way according to the band at 2956 and 2856 cm^{-1} attributed to molecular CH_3OH.

Figure S3_A – Effect of reaction time on FU conversion and products selectivity for $FeVO_4$ catalyst. Feed composition: FU 1%, CH_3OH 10%, N_2 89%; Pressure 1 atm, Temperature 300°C, overall gas residence time 1.0 s. Legend: ♦ FU conversion, ■ MF selectivity, ■ DMF selectivity, ■ VINFU selectivity, ■ C-loss.

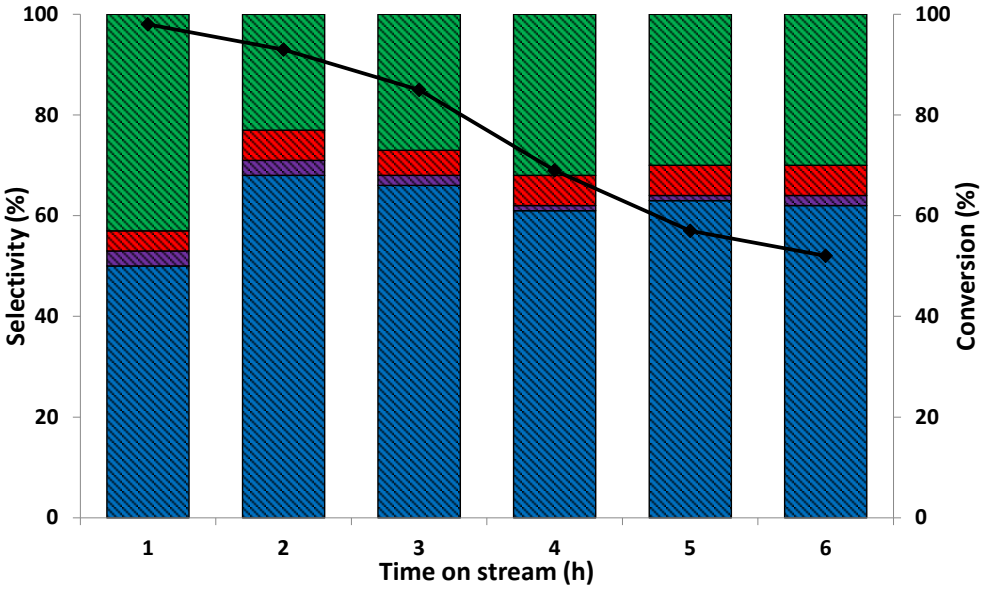


Figure S3_B – Effect of reaction time on FU conversion and products selectivity for $FeVO_4$ catalyst. Feed composition: FU 1%, CH_3OH 10%, N_2 89%; Pressure 1 atm, Temperature 350°C, overall gas residence time 1.0 s. Legend: ♦ FU conversion, ■ MF selectivity, ■ DMF selectivity, ■ VINFU selectivity, ■ C-loss.

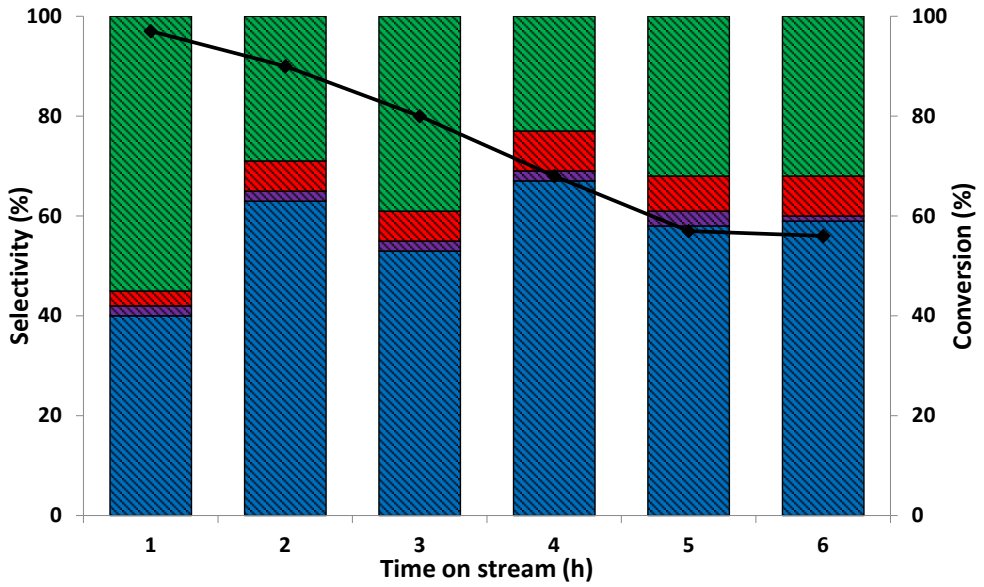


Figure S4 – Raman spectrum collected on $FeVO_4$ used at 320°C. The characteristic D3 band at 1600 cm^{-1} confirmed the presence of amorphous carbonaceous deposits over the surface of the catalyst.

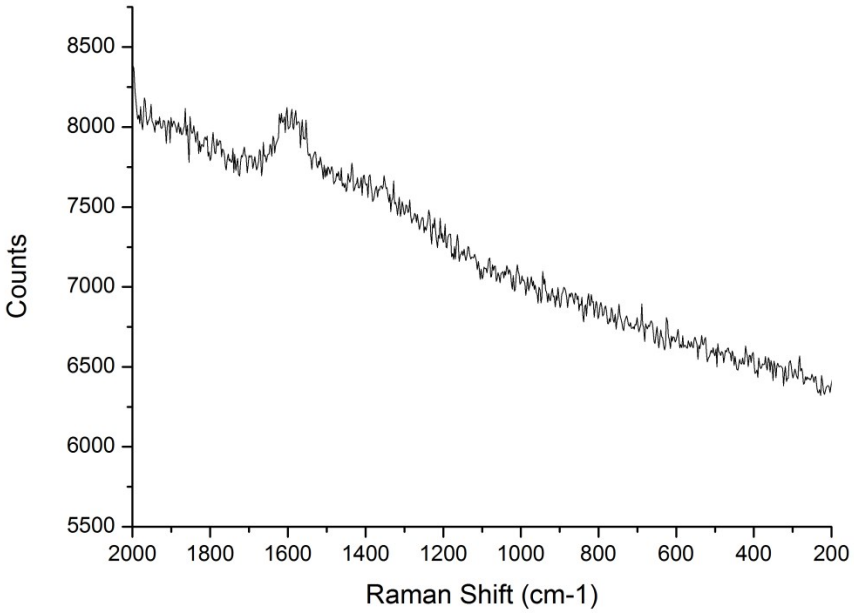


Figure S5 – $FeVO_4$ catalyst. Number of moles of gas formed, based on time, in the reaction of FU reduction with methanol at 320°C (solid line) and 250°C (dashed line). Feed composition: FU 1%, CH_3OH 10% , N_2 89% ; Pressure 1 atm, overall gas residence time 1,0 s. Legend: ♦ CO, ■ CO_2, ▲ CH_4, ● H_2.

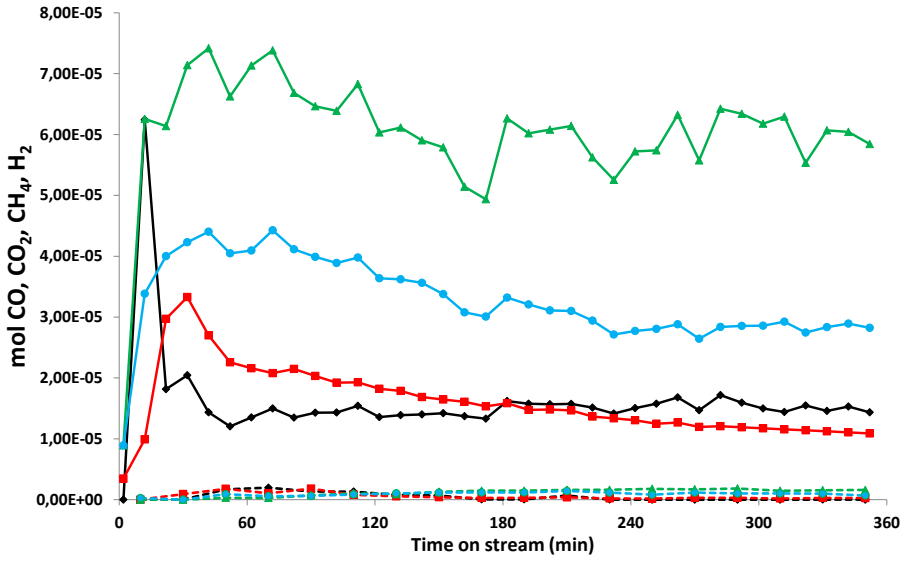


Figure S6 – $FeVO_4$ catalyst. Number of moles of gas formed, based on the time, in the reaction of methanol decomposition at 320°C (first hour) and in the reaction of FU reduction with methanol at 320°C. Feed composition: FU 1%, CH_3OH 10% , N_2 89% ; Pressure 1 atm, overall gas residence time 1,0 s. Legend: ♦ CO, ■ CO_2, ▲ CH_4, ● H_2.

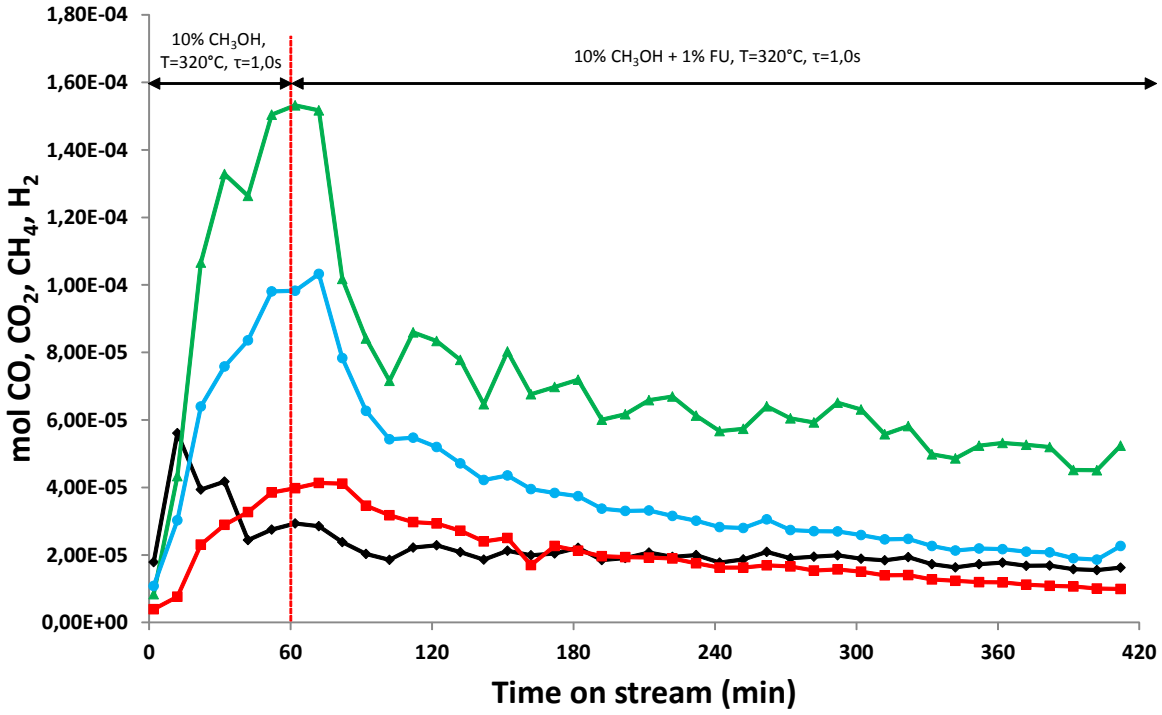


Figure S7_A – $FeVO_4$ catalyst. Methanol conversion and light compounds yield, based on the time, in the reaction of methanol decomposition at 320°C. Feed composition: FU 1%, CH_3OH 10% , N_2 89% ; Pressure 1 atm, overall gas residence time 1,0 s. Legend: ■ CH_3OH conversion, ♦ CO, ▲ CO_2, ■ CH_4, ♦ H_2, ● H_2O.

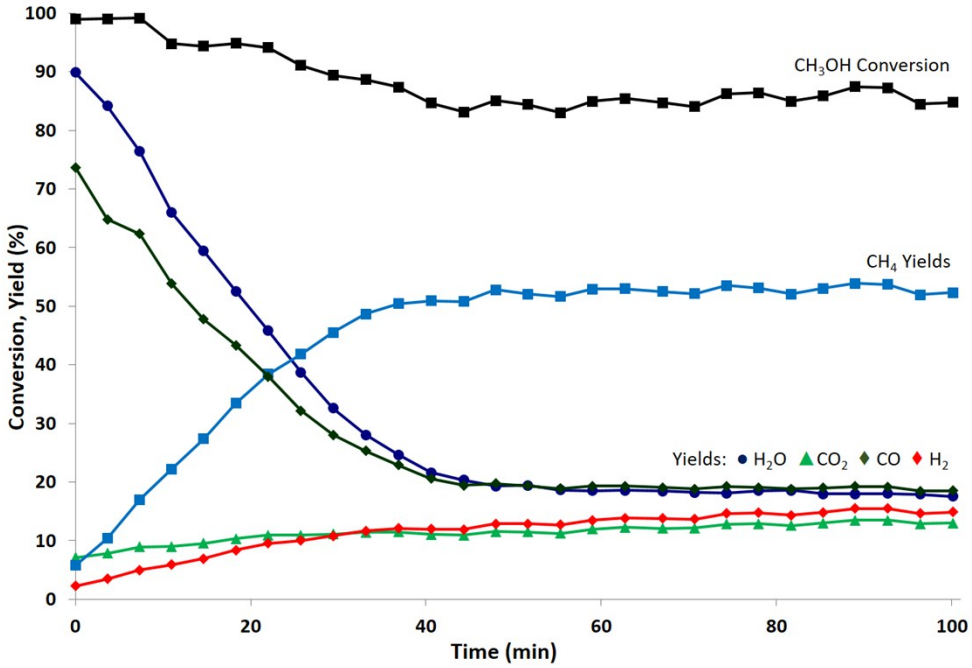


Figure S7_B – $FeVO_4$ catalyst. Reduction degree, based on time, obtained by-means of the oxygen balance.

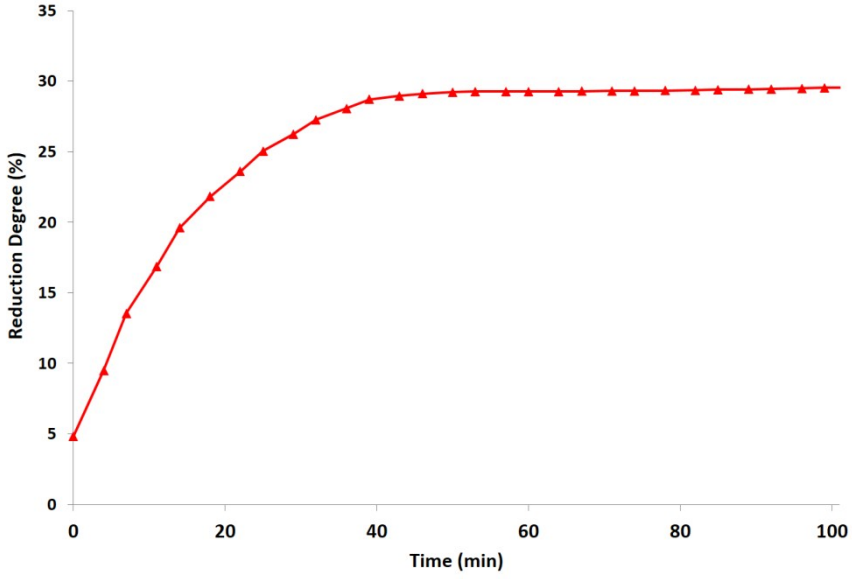


Figure S8 – $FeVO_4$ catalyst. Number of moles of gaseous products formed, based on the time, for the catalytic test performed feeding only FU over pre-reduced catalyst. Feed composition: FU 1%, N_2 99% ; Pressure 1 atm, Temperature 320°C, overall gas residence time 1,0 s. Legend: ♦ CO, ■ CO_2, ▲ CH_4, ● H_2.

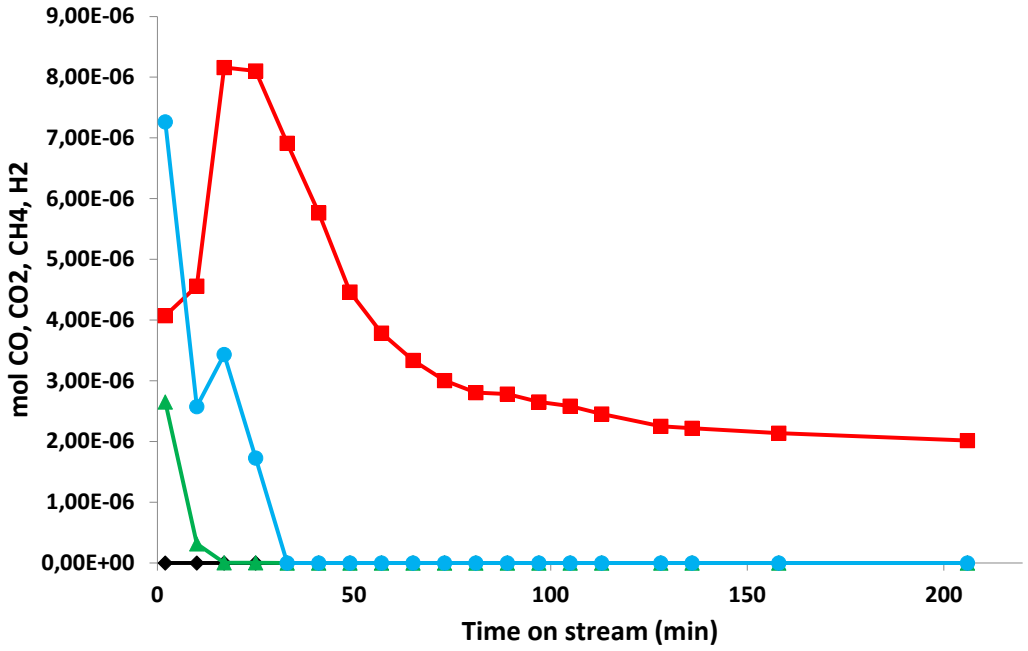


Figure S9 – Thermogravimetric (—) and differential thermal (—) analysis (TGA/DTA) in air of spent FeVO4 used in the catalytic test performed feeding only 1% mol of FAL at 320°C. The weight loss of ≈ 3% registered in the range of temperature between 290 and 360°C coupled with an exothermic DTA peak, well agree with the combustion of the carbonaceous deposits that derive from the decomposition of FAL.