Low Temperature Catalytic Oxidation of Ethanol Using Ozone over Manganese Oxide-Based Catalysts in Powdered and Monolithic Forms

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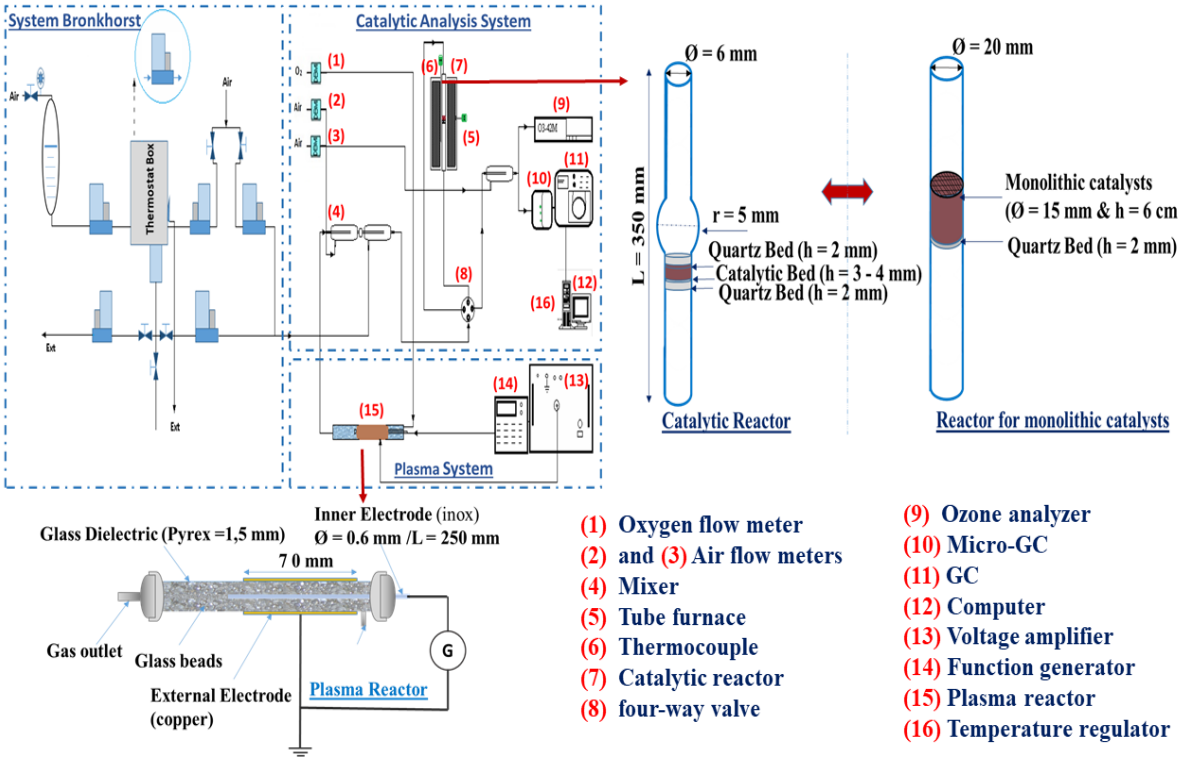
Electronic Supporting Information

by a 20 min purge with air after 3 h of reaction. Then reaction change from ozone decomposition to the oxidation of ethanol using ozone over the same 5Mn-Ti/FM monolithic catalyst, showing the conversion of ethanol and ozone (Total flow rate = 500 mL min^{-1}, [EtOH]=10 ppm, [O_3] = 70 ppm, T = 60 °C). **P8**

Experimental setup and reaction procedure



Scheme S1: Experimental setup.

The liquid VOC (i.e. ethanol) is introduced into a Bronkhorst evaporating system and mixed with an air flow. The desired concentration of ethanol is fixed at 10 ppm. It was obtained by diluting the initial ethanol flow with an air flow rate of 350 ml min^{-1}.

The generator used for the production of O_3 is a laboratory-scale plasma reactor of cylindrical geometry. It is made of glass, 20 mm in diameter and 400 mm in length. It consists of a stainless-steel electrode (a rod 250 mm in length and 0.6 mm in diameter) placed in the middle of the reactor and a second cylindrical copper electrode 70 mm in length surrounding the reactor. This electrode is connected to the ground. The reactor is filled with glass beads (ϕ = 2 mm) and ozone is generated from a stream of pure oxygen. The power supply is provided by a high voltage amplifier (frequency = 100 Hz and voltage = 20 kV) driven by a function generator providing a sinusoidal current that permits the output voltage to be controlled in the range of 0 to 20 kV.

The catalytic experiments on the powdered catalysts were carried out in a glass reactor. The catalyst was placed in the middle of the reactor and maintained by two 5 mm plugs of glass wool. The reactor is placed in a tubular furnace which accurately controls the reaction temperature at 60 °C. The catalytic tests on cordierite monoliths were carried out under the same operating conditions in a glass reactor equipped with quartz frit serving as support for the monolith. Reactor details are available on Scheme 1.

Table S1
Textural properties of the TiO_2mM support and the corresponding supported Mn and Pd catalysts (all calcined at 400 °C).

Catalysts	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)
TiO_2mM	136	0.25
5Mn/TiO_2mM	123	0.22
10Mn/TiO_2mM	113	0.20
20Mn/TiO_2mM	91	0.14
0.5Pd-5Mn/TiO_2mM	86	0.20

Table S2

Characteristics of the monolith catalysts (F_M: full monolith = 54 channels; P_M: partially plugged monolith = 16 channels).

Catalyst	TiO_2 (wt%)	Mn (wt%)*	Pd (wt%)*	Active channels
Ti/**F_M**	14	0	0	54
Ti/**P_M**	14	0	0	16
5Mn-Ti/**F_M**	14	5	0	54
5Mn-Ti/**P_M**	14	5	0	16
0.5Pd-5Mn-Ti/**F_M**	14	5	0.5	54
0.5Pd-5Mn-Ti/**P_M**	14	5	0.5	16

*Expected values

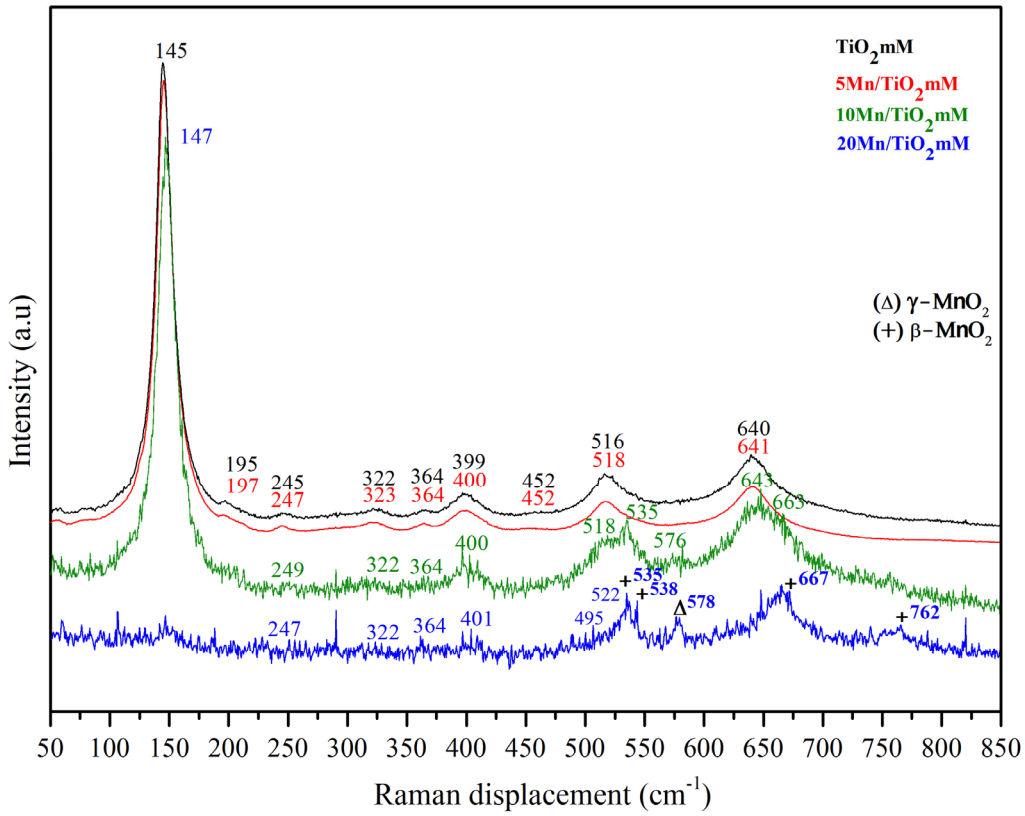


Figure S1: Raman spectra of the meso-macrostructured TiO_2mM support and the corresponding supported Mn/TiO_2-mM samples (5, 10 and 20 Mn wt%).

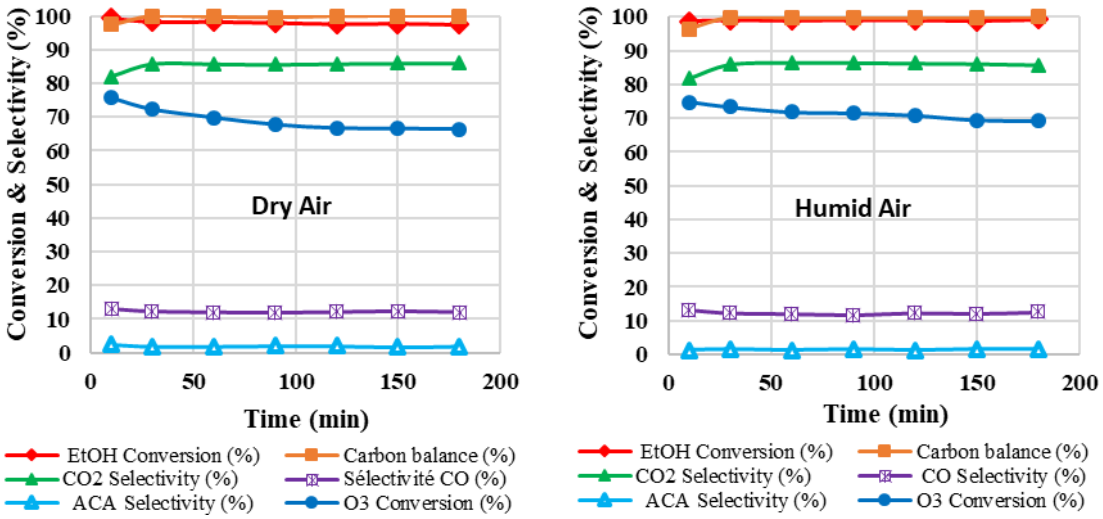


Figure S2: Ethanol conversion, ozone conversion, products selectivity and carbon balance as a function of time on stream in dry (left) and humid (right) conditions (catalyst = 20 mg, total flow rate = 500 mL min^{-1}, [EtOH]=10 ppm, [O_3] = 70 ppm, T = 60 °C) for the 10Mn/TiO_2 mM catalyst calcined at 400 °C.

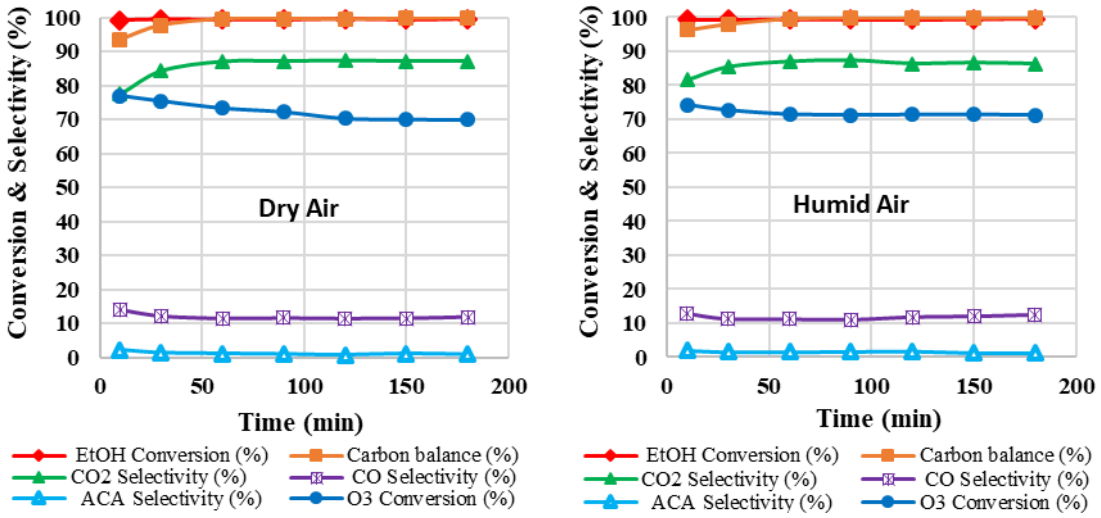


Figure S3: Ethanol conversion, ozone conversion, products selectivity and carbon balance as a function of time on stream in dry (left) and humid (right) conditions (catalyst = 20 mg, total flow rate = 500 mL min^{-1}, [EtOH]=10 ppm, [O_3] = 70 ppm, T = 60 °C) for the 20Mn/TiO_2 mM catalyst calcined at 400 °C.

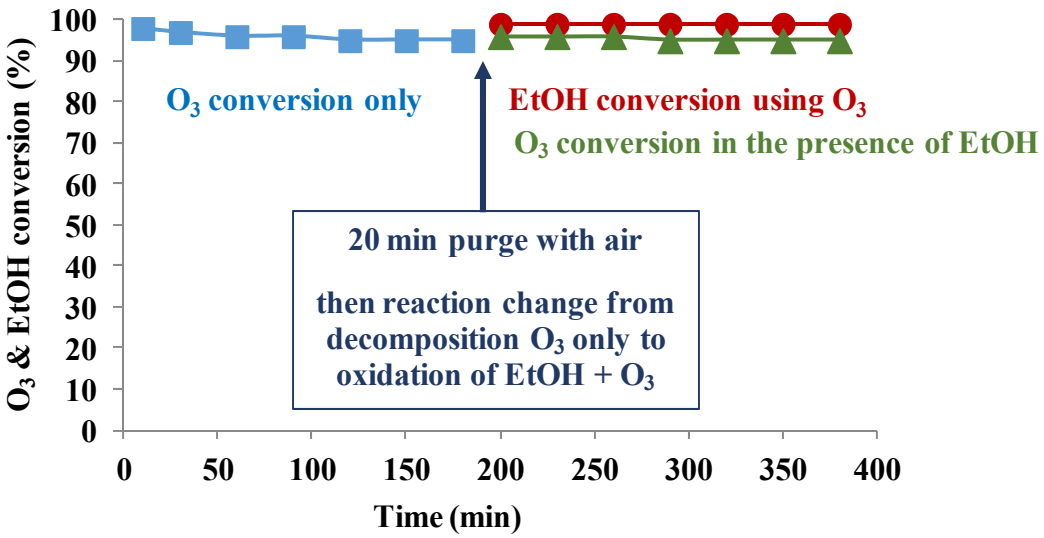


Figure S4: Ozone conversion as a function of time on stream in dry conditions over the manganese-impregnated full monolithic catalyst 5Mn-Ti/**FM** with 54 channels ([O_3] = 70 ppm, T = 60 °C), followed by a 20 min purge with air after 3 h of reaction. Then reaction change from ozone decomposition to the oxidation of ethanol using ozone over the same 5Mn-Ti/**FM** monolithic catalyst, showing the conversion of ethanol and ozone (Total flow rate = 500 mL min^{-1}, [EtOH]=10 ppm, [O_3] = 70 ppm, T = 60 °C).