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

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Abstract: Catalytic oxidation of low concentrations of ethanol was investigated in dry and humid air streams at low temperature (60 °C) over manganese oxide-based catalysts supported on a meso-macrostructured TiO₂ using ozone as the oxidant. Ethanol was selected as a representative model VOC present in indoor air, and its concentration was fixed to 10 ppm. For that purpose, a series of Mn/TiO₂ powder and monolithic catalysts was prepared, some doped with 0.5 wt% Pd. Whatever the catalyst, the presence of water vapor in the gas phase had a beneficial effect on the conversion of ethanol and ozone. The Pd-Mn/TiO₂ catalyst containing 0.5 wt% Pd and 5 wt% Mn exhibited superior oxidation efficiency to the Mn/TiO₂ counterparts by increasing ozone decomposition (77%) while simultaneously increasing the selectivity to CO₂ (85%). The selectivity to CO₂ approached nearly 100% by increasing the amount of catalyst from 20 to 80 mg. In a further step, alumina wash-coated cordierite honeycomb monoliths were coated with the 0.5Pd-5Mn/TiO₂ catalyst. Full conversion of ethanol to CO₂ without residual O₃ emitted (less than 10 ppb) could be attained, thereby demonstrating that the proposed Pd-Mn/TiO₂ monolithic catalyst fulfills the specifications required for onboard systems.

Keywords: VOCs; ozone; TiO₂; manganese oxide; cordierite monolith support



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1. Introduction

The quality of indoor air (homes, offices, vehicles, transportation, etc.) is a major concern for public health, as well as for better comfort and quality of life. Many pollutants present in indoor air can come from outside (polluted environment, proximity to traffic lanes, etc.) [1,2] or from the room itself due to the presence of synthetic materials, paints, use of cosmetics or cleaning products as well as human activities [3–7]. Volatile organic compounds, commonly referred to as VOCs, are among the main chemical species with nitrogen oxides (NO_x) and sulfur oxides (SO_x) involved in air pollution. VOCs can originate from many sources, including the natural environment (e.g., vegetables, endogenous VOCs) but mostly have an anthropogenic origin arising from a broad variety of human activities (e.g., mobile sources and industrial emissions) [7–9]. The degradation of these (toxic) atmospheric pollutants has then become a major area of concern in environmental protection. The direct effects of low concentrations of VOCs on human health are still poorly understood due to the lack of data. Benzene has been shown to provoke gene mutations and leukemia, while butadiene and benzene have also been linked with cancer. VOCs have been implicated in photochemical pollution, leading to an increase in tropospheric ozone [10,11] and formation of toxic mists (smog) [11]. This is a very commonly observed phenomenon

due to fine particulate matter (**PM**) atmospheric pollution, causing respiratory diseases to exposed people [11]. When combined with VOCs, the inhalation of **PM** promotes the penetration of VOCs into the respiratory tract, thereby increasing their toxicity [10].

The traditional technologies for VOC removal from the polluted air stream are based on non-destructive (recovery) [12–16] or destructive treatments [17–29]. Non-destructive treatments essentially include adsorption of VOCs onto porous materials such as activated carbons or zeolites. These processes are efficient at ambient temperature, but they have strong limitations due to frequent regenerations or replacements of adsorbents, resulting in important costs. Many advanced processes (destructive treatments) have been developed for the degradation of VOC pollutants to relatively harmless compounds or even to their complete oxidation to CO₂ and H₂O, including among others, photocatalysis, catalytic oxidation, catalytic ozonation and non-thermal plasma catalysis [30]. Photocatalysis can operate at room temperature [31]. However, it is not well-adapted for one pass treatment of high flow rate of indoor air at a low VOC concentration levels, due to too low reaction kinetic rates. Catalytic oxidation with air or oxygen as oxidant needs high temperatures to be efficient, thereby leading to higher energy costs when large flow rates have to be treated. Such drawbacks can be circumvented by using noble metal-based catalysts for the complete oxidation of VOCs at a lower temperature [32]. Noble metals combined with non-precious transition metal oxides also show excellent catalytic activities in VOC degradation, as shown by Zhang et al. with Pd/Al₂O₃–CuO catalysts [33]. In addition to noble metals whether or not combined with non-precious metal oxides, transition metal oxides alone have also been extensively studied for application in VOC elimination in the temperature range 150–200 °C (e.g., ordered mesoporous MnO₂ [34], Mn₃O₄, Mn₂O₃, SmMn₂O₅ [35]).

Among the available VOC removal technologies, catalytic oxidation using ozone is recognized as an alternative and effective process particularly suited for the oxidation of volatile organic compounds at temperatures far lower than those used for conventional catalytic oxidation reactions [36–38]. Huang and co-workers comprehensively reviewed very recently the advances made in the catalytic oxidation of a variety of VOCs (oxygenated, chlorinated, aromatic and sulfur-containing VOCs) over different catalysts using ozone at low temperature [39]. They showed that this promising technology is well suited for VOC removal at low concentrations. Widespread application of ozone in the treatment of VOCs emitted by industrial processes or present in indoor environments is thus expected to occur in the near future [39]. Ozone is easily produced by flowing air or pure oxygen through a non-thermal plasma reactor [40,41]. Recently, many studies have been focused on unsupported or supported manganese oxides as efficient catalysts for the oxidation of VOCs using ozone as oxidant. Highly active oxygen species are formed by decomposition of ozone on MnO_x oxides (peroxide species), which can further oxidize VOCs at lower reaction temperatures than with oxygen. The apparent activation energy of the total oxidation of VOCs can be reduced with ozone compared to that under oxygen, thereby decreasing the reaction temperature to 100 °C or even less [30,42]. Oyama and co-workers have also shown that manganese oxide-based catalysts have the highest activity compared with transition metal oxides based on Fe, Mo, Co, Cu, Ni, Ce and V [42,43]. The efficiency of manganese oxides (MnO_x) dispersed on different supports was investigated for the catalytic oxidation of formaldehyde [44], acetone [45,46], cyclohexane [47,48], benzene [49–51], toluene [52–54] and chlorobenzene [55] by ozone. The group of Oyama [56,57] examined the ethanol oxidation using ozone over alumina and silica supported manganese and molybdenum oxide catalysts in the temperature range of ~27 °C to ~277 °C for a high ethanol concentration (0.8 mol%). They showed that for all catalysts, ethanol was found to react with ozone at lower temperatures than with oxygen, in agreement with the stronger oxidizing ability of ozone compared to oxygen, and with lower activation energy. The main oxidation product was CO₂ over the supported MnO_x catalysts, while for the supported molybdenum oxides, the selectivity was mainly to acetaldehyde (other products being ethylene, ethyl acetate and diethyl ether).

The present work aims at investigating the low temperature catalytic oxidation of low concentrations of VOCs over manganese oxide-based catalysts supported on titania using ozone. Ethanol was selected as the representative model VOC present in indoor air (rooms or vehicles). In order to optimize the dispersion of the active phase on the support and increase the gas–solid contact, a hierarchical meso–macroporous titanium dioxide with high surface area was successfully synthesized and further used as support for the manganese oxide active phase, possibly doped with palladium (0.5 wt%). In the next step, we examined the scaling of laboratory experiments for an onboard application in transportation vehicles. For that purpose, cordierite honeycomb monoliths were used as support for the impregnation of the Mn/TiO₂mM and Pd–Mn/TiO₂ catalysts. Several techniques were employed to characterize the structural, textural and surface properties of the powder and monolithic catalysts. Secondly, low temperature ozonation (60 °C) of low ethanol emissions (10 ppm) was carried out over all investigated catalysts under dry and humid air streams. Emphasis was also put on the evaluation of the catalysts to reach full ethanol conversion while simultaneously achieving complete ozone decomposition, so as to fulfill the specifications required for onboard systems.

2. Results and Discussion

2.1. Characterization of Powder Catalysts

2.1.1. Chemical Analysis by ICP-OES

Table 1 gives the sample labels and the manganese content (target and measured values) of the Mn/TiO₂mM catalysts calcined at various temperatures. The Pd content of the corresponding Pd–Mn/TiO₂mM counterpart is also shown in Table 1. Good agreement was observed between the desired and measured Mn and Pd values for all supported catalysts. The loading of manganese and palladium was very close to the one expected. The slight differences observed may be due to the impregnation process that was carried out in aqueous solution and not under incipient wetness conditions.

Table 1. Labels and expected and measured (ICP) chemical composition of the catalysts in powdered form.

Catalyst	Mn (wt%)		Pd (wt%)		Calcination Temperature (°C)
	Expected	Measured	Expected	Measured	
TiO ₂ mM	-	-	-	-	400
5Mn/TiO ₂ mM-400	5	4.56	-	-	400
5Mn/TiO ₂ mM-300	5	4.62	-	-	300
5Mn/TiO ₂ mM-200	5	4.85	-	-	200
10Mn/TiO ₂ mM-400	10	9.74	-	-	400
20Mn/TiO ₂ mM-400	20	18.40	-	-	400
0.5Pd–5Mn/TiO ₂ mM	5	4.71	0.5	0.46	400

2.1.2. XRD Analysis

The evolution of the structural signature of the Mn/TiO₂mM catalysts calcined at 400 °C as a function of the manganese content is presented in Figure 1, in comparison with the X-ray diffractogram of the meso–macrostructured titanium oxide support.

The meso–macroporous TiO₂ sample showed the characteristic diffraction pattern of anatase, as well as traces of the brookite variety. Reference X-ray lines attributed to pyro-lusite MnO₂ (JCPDS card 98-024-6888) and to bixbyite Mn₂O₃ (JCPDS card 98-004-3464) are shown at the bottom of Figure 1. After impregnation of 5 wt% of manganese (5Mn/TiO₂mM sample), only the crystalline phase of anatase was detectable, along with traces of brookite. No XRD reflections corresponding to manganese oxides could be evidenced for the sample with the lowest Mn content of the series, thereby suggesting the excellent dispersion of Mn in the meso–macrostructured TiO₂ support. For the samples containing 10 wt% and 20 wt% Mn, additional lines were observed, which are associated with the presence of

manganese oxides. However, the comparison of the XRD patterns of the 10Mn/TiO₂mM and 20Mn/TiO₂mM samples with the reference MnO₂ (pyrolusite) and Mn₂O₃ (bixbyite) did not allow us to distinguish between either manganese oxide phases. Part of the XRD reflections of MnO₂ and Mn₂O₃ were overlapped with that of the meso–macrostructured TiO₂ support (anatase phase), thereby preventing us from providing a more detailed analysis of the Mn/TiO₂mM samples (≥ 10 wt% Mn). Regarding the palladium–manganese supported TiO₂ sample (0.5Pd–5Mn/TiO₂mM), no additional lines corresponding to PdO (or PdOx phase) could be detected. The XRD pattern of the 0.5Pd–5Mn/TiO₂mM was found similar to that of the analogous palladium-free 5Mn/TiO₂mM sample.

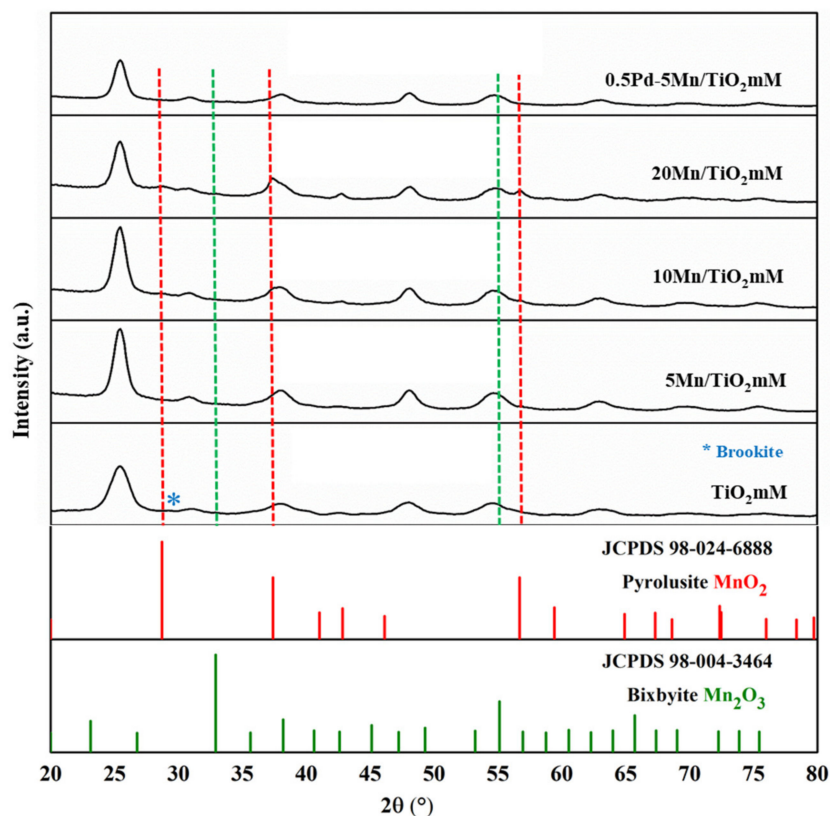


Figure 1. Wide-angle XRD patterns of the hierarchical meso–macrostructured TiO₂mM support and the corresponding supported Mn and Pd samples (all calcined at 400 °C). Bottom: JCPDS references MnO₂ and Mn₂O₃.

2.1.3. Textural Properties by Physisorption of Dinitrogen at 77 K

The N₂ adsorption–desorption isotherms of the meso–macrostructured TiO₂ support and the manganese-supported samples (5, 10 and 20 wt% Mn) are shown in Figure 2.

According to the IUPAC classification, all isotherms were of Type IVa, corresponding to mesoporous materials [58]. Capillary condensation was accompanied by hysteresis, which started to occur for pores wider than 4 nm [58]. These isothermal curves also exhibited a long saturation plateau at high relative pressures. The hysteresis loops were of Type H1, readily attributed to the presence of uniform mesopores with a narrow range. All manganese-based samples exhibited a very similar hysteresis shape, thereby indicating that the size distribution of the mesopores was very close, whatever the Mn loading. A slight decrease of the mean pore size was however observed when increasing the Mn content, from 6.3 nm for the TiO₂mM and 5Mn/TiO₂mM samples to 5.6 nm for the sample with the highest Mn loading (20Mn/TiO₂mM). The specific surface areas and pore volumes of the parent meso–macrostructured titania and the corresponding Mn/TiO₂mM and Pd–Mn/TiO₂mM samples are summarized in Table S1 (ESI). The TiO₂mM support exhibited a surface area of 136 m²·g^{−1} coupled to a pore volume of 0.25 cm³·g^{−1}. As

expected, with impregnation of manganese or after successive impregnations of Mn and Pd followed by calcination, a progressive decrease of adsorbed nitrogen and surface area was observed for all Mn/TiO₂mM (Figure 2) and Pd–Mn/TiO₂mM samples when compared to the parent TiO₂ support. The pore volume of the Mn and Pd samples was however less prone to change (slight decrease from 0.25 to 0.20 cm³·g^{−1}), except for the sample with the highest Mn content (20Mn/TiO₂mM), in agreement with its concomitant decrease of surface area and mesopore size.

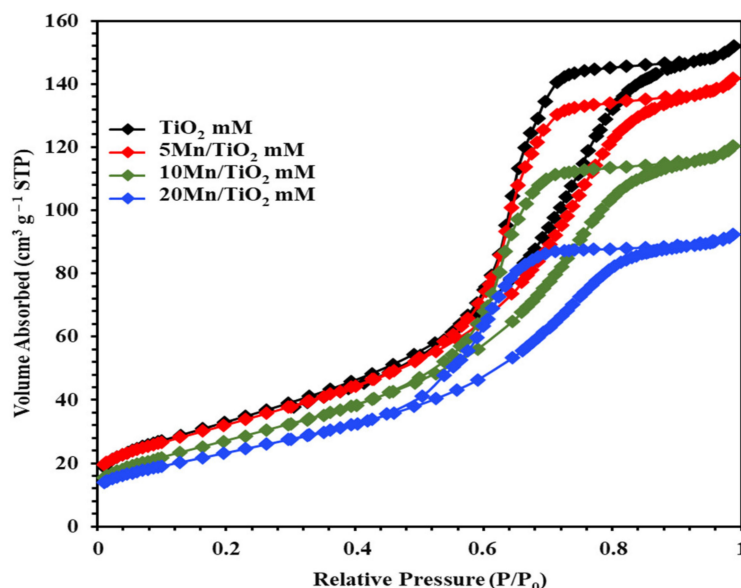


Figure 2. N₂ adsorption–desorption isotherms for the meso–macrostructured TiO₂mM support and the corresponding supported Mn/TiO₂mM samples (5, 10 and 20 Mn wt%).

Note that the macroporous part of the 0.5Pd–Mn/TiO₂mM sample could not be visualized on the nitrogen adsorption–desorption isotherms because of their large dimensions (2.3 µm as determined by mercury porosimetry).

2.1.4. Raman Analysis

In the next step, the Mn/TiO₂mM samples were investigated by Raman spectroscopy. The aim was to gain better insight into the nature of the manganese oxide supported on the titania support. Raman analysis confirmed the observations made previously by XRD for the parent meso–macrostructured support and the 5Mn/TiO₂mM sample (Figure S1—ESI). First, the characteristic peaks of the anatase phase of the TiO₂mM support were observed at 147 cm^{−1} (symmetric stretching vibration of O–Ti–O), 195 cm^{−1}, 399 cm^{−1} (symmetric bending vibration of O–Ti–O), 516 cm^{−1} (antisymmetric bending vibration of O–Ti–O) and 640 cm^{−1}, corresponding to the Eg(1), Eg(2), B1g(1), (A1g + B1g(2)) and Eg(2) modes, respectively [59]. The characteristic peaks of the trace brookite phase were detected at 245, 322 and 364 cm^{−1}. Next, the Raman spectrum of the sample containing the lowest amount of manganese (5Mn/TiO₂mM) was found to be similar to that of the hierarchical TiO₂ support. No shift characteristic of the Raman signature of manganese oxide could be detected, in agreement with the data obtained by XRD. When comparing the 5Mn/TiO₂mM compound with the one containing 10 wt% of Mn, slight changes could be seen on the Raman spectrum of the 10Mn/TiO₂mM sample. The absorption band located at 643 cm^{−1} became broader, and the band at 518 cm^{−1} also showed a shoulder around 535 cm^{−1}. These bands could correspond to the signature of manganese oxide of the β-MnO₂ variety. Additional absorption bands were also observed on the spectrum of the 20Mn/TiO₂mM sample compared with the 5Mn/TiO₂mM compound, possibly corresponding to two different MnO_x types. Vibration bands of the β-MnO₂ variety were seen at 535–538 cm^{−1}, 667 cm^{−1} and 762 cm^{−1} on the Raman spectrum of the 20Mn/TiO₂mM sample [60,61].

The peak appearing at 578 cm^{-1} was due to the $\gamma\text{-MnO}_2$ variety and was observed for the sample with the highest manganese content (20Mn/TiO₂mM) and possibly also for the 10Mn/TiO₂mM sample to a lesser extent.

2.1.5. H₂-TPR Analysis

Redox properties of catalysts are important factors affecting the oxidation activity. The oxidation and reduction behavior of the 5Mn/TiO₂mM series calcined at different temperatures (200, 300 and 400 °C) was investigated by H₂-TPR, as displayed in Figure 3. Such a commonly used technique can bring information on the oxidation state of the manganese oxide and hence provide a better identification of the MnOx phases present in the samples with the lowest Mn content (5 wt%).

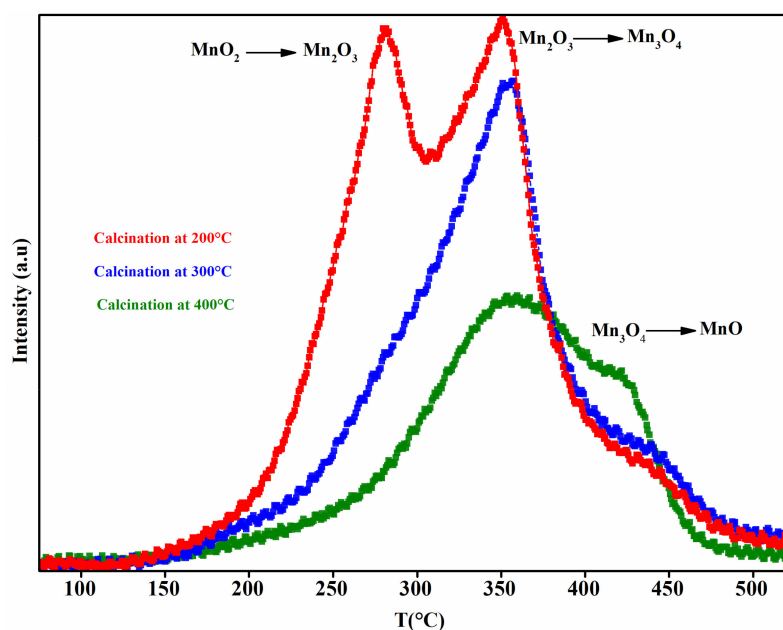


Figure 3. H₂-TPR profiles of the 5Mn/TiO₂mM samples calcined at various temperatures (200, 300 and 400 °C).

There was a marked difference between the TPR profiles of each of the 5Mn/TiO₂mM samples. The H₂ reduction profile of the sample calcined at 200 °C was mainly composed of two signals, the second one being asymmetric. Then the TPR curve ended with a shoulder above 430 °C. The first reduction peak centered at 260 °C could be attributed to the reduction of MnO₂ to Mn₂O₃ [62,63]. Then Mn₂O₃ was reduced into Mn₃O₄ (second peak with a maximum at 350 °C), followed by the formation of MnO (shoulder) [64]. Such behavior is in agreement with what is reported in the literature for supported manganese oxide catalysts. The reduction of MnO₂ to Mn₂O₃/Mn₃O₄ then to MnO leads to the formation of two main peaks in the TPR profile [55,64]. The reduction profile of the sample calcined at 300 °C exhibited an asymmetric peak with a maximum at 350 °C (Mn₂O₃ to Mn₃O₄), along with a similar shoulder as that observed for the sample calcined at the lowest temperature (Mn₃O₄ to MnO). A closer look at the reduction profile indicated the presence of a small shoulder at around 270 °C that could readily be attributed to the reduction of residual MnO₂ to Mn₂O₃. The reduction of the 5Mn/TiO₂mM sample calcined at 400 °C occurred in two steps. The main TPR peak centered at 350 °C again corresponded to the reduction of Mn₂O₃ to Mn₃O₄, while the second signal originated from the reduction of Mn₃O₄ to MnO. According to the H₂ uptake between 100 and 500 °C, the relative amount of Mn^{IV} and Mn^{III} in the 5Mn/Ti samples calcined at various temperatures could be estimated. The results shown in Table 2 indicate that manganese was almost exclusively present as Mn^{IV} in the sample calcined at the lowest temperature (200 °C). By contrast, the corresponding 5Mn/TiO₂mM calcined at 400 °C was mainly composed of Mn^{III} (as supported Mn₂O₃ phase). Among this series,

such catalyst exhibited the highest conversion and selectivity to CO₂ in the low-temperature oxidation of ethanol using ozone, as is shown below in Section 2.2. As a result, a calcination temperature of 400 °C was selected for all the (Pd)Mn/TiO₂mM catalysts.

Table 2. Relative amount in percent of MnO₂ and Mn₂O₃ in the Mn/TiO₂mM samples calcined at various temperatures.

Sample	Calcination Temperature (°C)	H ₂ Consumption (cm ³ H ₂ /g STP)	% MnO ₂ (as % Mn ^{IV})	% Mn ₂ O ₃ (as % Mn ^{III})
5Mn/TiO ₂ mM-200	200	20.6	94	6
5Mn/TiO ₂ mM-300	300	14.1	39	61
5Mn/TiO ₂ mM-400	400	11.4	14	86
10Mn/TiO ₂ mM-400	400	28.9	40	60
20Mn/TiO ₂ mM-400	400	61.0	51	49

The information in Table 2 also revealed that an increase in the Mn loading from 5 to 20 wt% (10Mn/Ti and 20Mn/Ti samples) led to a decrease of the Mn^{III}/Mn^{IV} ratio.

2.2. Catalytic Activity

2.2.1. Catalytic Oxidation of Ethanol with Catalysts in Powder Form

Blank oxidation experiments were first performed (i) with ozone in the absence of any catalyst, and (ii) without ozone in the presence of the 5Mn/TiO₂mM catalyst and molecular oxygen, in order to confirm that there was no significant ethanol conversion.

Case of the 5Mn/TiO₂mM Catalyst

The manganese-impregnated TiO₂mM catalyst containing 5 wt% Mn was first calcined at different temperatures (200 and 400 °C). The resulting 5Mn/TiO₂mM-200 and 5Mn/TiO₂mM-400 samples were evaluated for their ability to oxidize ethanol into CO₂ with ozone under dry and humid air streams. Results are shown in Table 3.

Table 3. Ethanol oxidation on the TiO₂mM, 5Mn/TiO₂mM and 0.5Pd–5Mn/TiO₂mM catalysts in powdered form, in dry and humid air (10%RH) conditions (catalyst = 20 mg, total flow rate = 500 mL min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C, Time = 3 h).

Catalyst	T Calc (°C)	Atm. (Air)	EtOH Conv. (%)	Selectivity (%)			O ₃ Conv. (%)
				CO ₂	CO	ACA ¹	
TiO ₂ mM	400	dry	73	61	6	33	12
5Mn/TiO ₂ mM	200	dry	86	67	18	15	53
5Mn/TiO ₂ mM		humid	90	73	16	11	52
5Mn/TiO ₂ mM	400	dry	95	83	9	8	64
5Mn/TiO ₂ mM		humid	99	85	13	2	65
10Mn/TiO ₂ mM	400	dry	97	86	12	2	66
10Mn/TiO ₂ mM		humid	99	86	12	2	69
20Mn/TiO ₂ mM	400	dry	100	87	12	1	70
20Mn/TiO ₂ mM		humid	100	86	13	1	71
0.5Pd–5Mn/TiO ₂ mM	400	dry	98	83	13	4	77
0.5Pd–5Mn/TiO ₂ mM		humid	99	85	12	3	76

¹ ACA = acetaldehyde.

Higher ethanol and ozone conversion, along with improved selectivity to CO₂, could be reached with the catalyst calcined at 400 °C with respect to that thermally treated at 200 °C. The O₃ conversion increased from 53% to 64% under dry air for 5Mn/TiO₂mM-200 and 5Mn/TiO₂mM-400, respectively. A more pronounced effect of the calcination temperature of the catalyst was noticed on the CO₂ selectivity (67% and 83%, respectively). Additionally, when the oxidation reaction was carried out under a humid air stream (RH = 10%), the ethanol conversion reached nearly 100%, with a slight increase in the selectivity to CO₂ and O₃ conversion compared to the dry conditions (Table 3, Figure 4). Note

that water vapor was shown to increase the oxidation efficiency whatever the calcination temperature of the 5Mn/TiO₂mM catalyst.

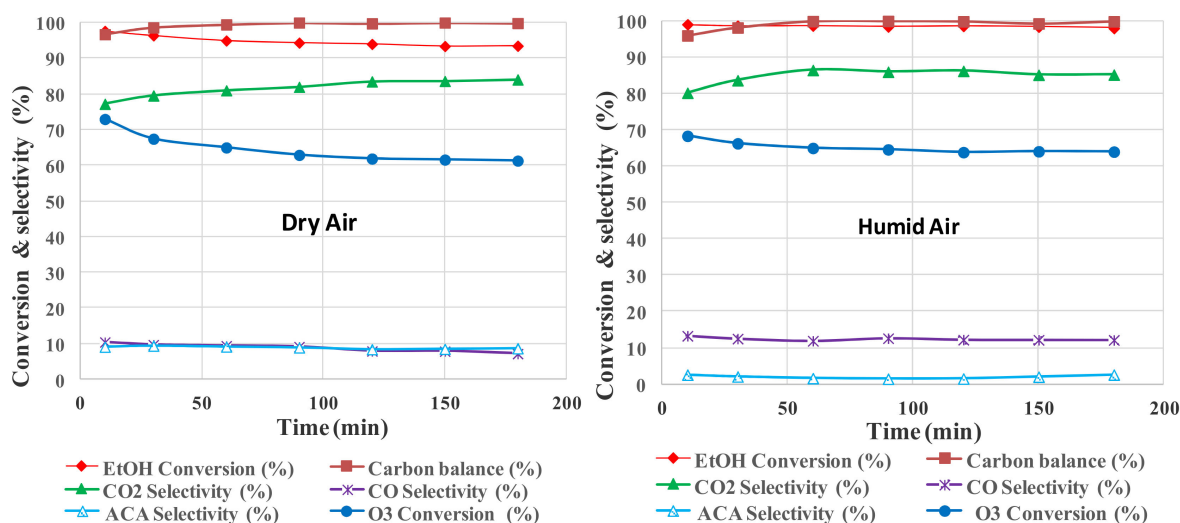


Figure 4. Ethanol conversion, ozone conversion, products selectivity and carbon balance as a function of time on stream in dry (left) and humid (right) conditions (catalyst = 20 mg, total flow rate = 500 mL·min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C) for the 5Mn/TiO₂mM catalyst calcined at 400 °C.

The influence of the manganese content on the catalytic performances was next examined under dry and humid conditions for the Mn/TiO₂mM calcined at 400 °C. The Mn content was varied between 5 and 20 wt%. For the sake of clarity, all samples are hereafter labeled as xMn/TiO₂mM with x = 5, 10 or 20 wt%. TiO₂mM support was also used for comparison purposes. The results are shown in Table 3 and Figures S2 and S3 (ESI). Although being active in the oxidation of ethanol using ozone (73% conversion and 61% selectivity to CO₂), the TiO₂mM support led to a very low conversion of ozone (12%).

By contrast, a larger increase in the catalytic performance was observed for all Mn/TiO₂mM samples compared to the titania support. Almost full ethanol conversion (92–100%), along with high ozone conversion values were reached in the dry air stream. One could notice a slight increase in the O₃ conversion (64–70%), most probably due to the increase in the conversion of ethanol for increasing manganese content. A significant enhancement in the selectivity to CO₂ was also observed with respect to the parent TiO₂mM (83–87% compared with 61%). Secondary by-products such as carbon monoxide and acetaldehyde were produced (13–15% as a whole). However, no other products were detected, and hence the carbon balance reached 100% for all catalysts.

Under the humid air stream, the 5Mn/TiO₂mM and 10Mn/TiO₂mM samples showed a slight increase in the conversion of ethanol and in the selectivity to CO₂ compared to the reaction performed under dry air conditions, thereby indicating a beneficial role of the relative humidity on the catalytic performances. Such a phenomenon was already reported for the oxidation of benzene with ozone over MnO_x/Al₂O₃ catalysts [40]. The addition of water vapor was shown to suppress deactivation of the catalysts by inhibiting accumulation of the byproducts on the catalyst surface and, hence, by promoting their oxidation. As a result, increased selectivity to CO₂ was observed in the presence of water vapor [40]. Additionally, the presence of water vapor in the reaction feed favored the formation of reactive hydroxyl groups [39] through the interaction of adsorbed water and atomic oxygen O* present on the catalyst surface (stemming from ozone decomposition on the catalyst as shown in Equation (1) and discussed in Section 2.3). Such abundant OH groups greatly promote VOCs oxidation, thereby resulting in improved VOCs conversion [39]. Our results are in full agreement with those found in the literature, since the highest conversion of

ethanol was achieved when the reaction was performed in the presence of water, whatever the catalyst manganese content (Table 3). A slight increase in the conversion of ozone was also observed during ethanol oxidation over the Mn-based catalysts in humid air compared to the dry air conditions (Table 3). For such humid conditions (RH = 10%), the adsorption of water on the surface active sites did not affect ozone adsorption and activation on the Mn/TiO₂mM catalysts. Zhu et al. [65] also reported that a high ozone decomposition rate was observed over α -MnO₂ when the relative humidity was low (5%). However, for higher RH, water adsorption on the active sites increased, leading to low ozone conversion by blocking of the surface active sites [65].

The evolution of ethanol and ozone conversion, product selectivity and carbon balance, as a function of time on stream in dry and humid conditions for the 5Mn/TiO₂mM catalyst, is shown in Figure 4. The higher EtOH and O₃ conversions under humid conditions than under dry air are clearly depicted in Figure 4. Moreover, the catalyst exhibited a stable activity as a function of time on stream under humid air.

Effect of Palladium Addition

Doping manganese-based catalysts by small amount of noble metals is known to improve VOC oxidation efficiency. We then investigated the influence of the presence of palladium as a doping element on the catalytic performance of the 5Mn/TiO₂mM samples (Table 3). Such a catalyst was selected with respect to the samples with higher manganese content, because it converted ethanol to CO₂ with virtually the same efficiency in terms of conversion and selectivity, under humid air than did the 10Mn/TiO₂mM and 20Mn/TiO₂mM catalysts.

As expected, addition of a small amounts of Pd led to an increased O₃ efficiency (Table 3, Figure 5). A higher ozone conversion was observed for the catalyst containing palladium (0.5Pd-5Mn/TiO₂mM) than for the Pd-free counterpart, even under humid conditions (77% and 76% under dry and humid air, respectively). Again, the stability of this 0.5Pd-5Mn/TiO₂mM catalyst was ascertained over more than three hours of reaction (Figure 5), thereby indicating that the blocking of the ozone reaction sites on the catalyst surface by molecular water adsorption did not occur. The beneficial effect of palladium on increasing the ozone decomposition efficiency in the presence of water was already mentioned by Dhandapani and Oyama [42].

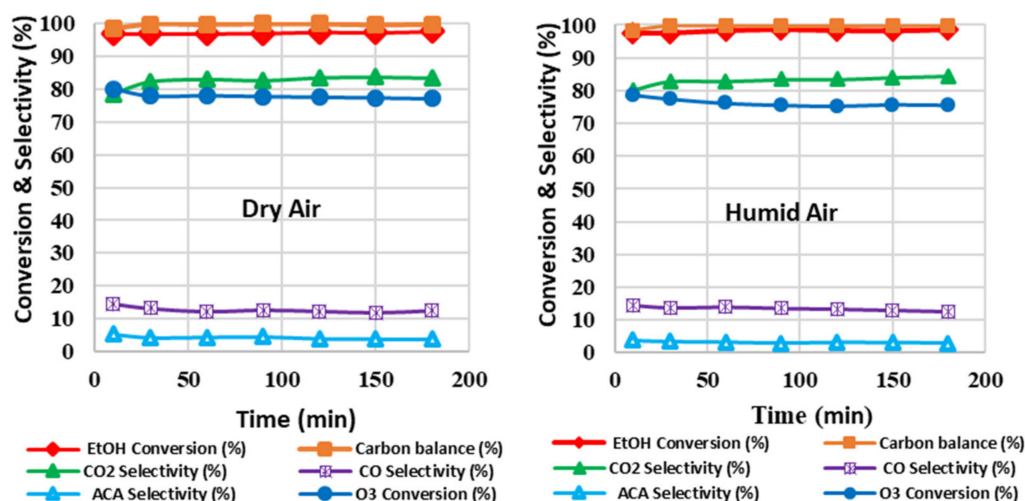


Figure 5. Ethanol conversion, ozone conversion, products selectivity and carbon balance as a function of time on stream in dry (left) and humid (right) conditions (catalyst = 20 mg, total flow rate = 500 mL·min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C) for the palladium-doped catalyst (0.5Pd-5Mn/TiO₂mM).

The effect of the residence time was next studied with the 0.5Pd–5Mn/TiO₂mM catalyst by varying the mass of catalyst in the 10–80 mg range (residence time from 1.2 to 9.6 ms), at a constant flow rate under dry and humid air stream. The results are shown in Figure 6. As expected, increasing the amount of catalyst resulted in a concomitant increase in the conversion of ethanol, which rapidly reached 100%, along with a simultaneous increase in CO₂ selectivity (91%) with 60 mg of catalyst under humid air. Moreover, acetaldehyde formation went to zero as a function of the residence time. These results show that the 0.5Pd–5Mn/TiO₂mM catalyst is highly active in the oxidation of ethanol using ozone, even for a mass of 20 mg. In addition to being capable of converting low ethanol concentration at low temperature with a rational use of ozone, the palladium doped 5Mn/TiO₂mM catalyst proved to be highly stable even under humid air.

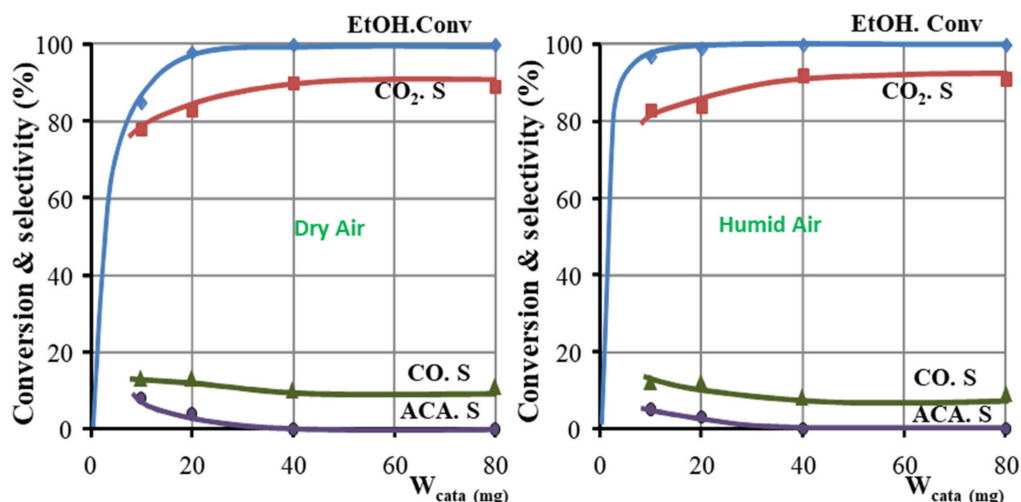


Figure 6. Influence of the mass of the 0.5Pd–5Mn/TiO₂mM catalyst in powdered form under dry and humid (RH = 10%) conditions ([EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C, Time = 3 h).

2.2.2. Catalytic Oxidation of Ethanol on Cordierite-Based Monoliths

In a further step, alumina wash-coated cordierite honeycomb monoliths were coated with the 5Mn/TiO₂mM and 0.5Pd–5Mn/TiO₂mM catalysts and compared with their powdered forms in the total oxidation of ethanol under dry and humid conditions. Bare cordierite honeycomb monoliths are colorless (Figure 7a), but after successive coatings of active catalysts, there was a drastic change in the color, which indicated that the surface of the monolith was entirely coated with the Pd–Mn/TiO₂mM catalyst, as illustrated in Figure 7b (case of 0.5Pd–5Mn–Ti/FM monolith). Table S2 (ESI) shows the monolith labels, the titania, manganese and palladium content as well as the number of active channels of the monolithic catalysts.

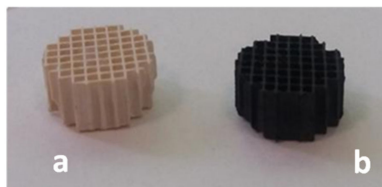


Figure 7. (a) Naked alumina wash-coated cordierite honeycomb monolith and (b) the corresponding monolith catalyst after impregnation with TiO₂ (14 wt%), Mn (5 wt%) and Pd (0.5 wt%).

The oxidation reaction was first performed with the cordierite monolithic catalysts containing **54 channels** (FM series). The same gas phase composition was used as for the catalysts in powdered form, with a total flow rate of 500 mL·min^{−1} corresponding to a residence time of 0.1 s.

A preliminary test was performed with the full monolith after impregnation with 14 wt% TiO₂ and 5 wt% Mn in the ozone decomposition reaction first (in the absence of ethanol). Figure S4 (ESI) shows the ozone conversion as a function of time on stream in dry conditions over the 5Mn-Ti/FM monolith. A high ozone conversion could be reached after 3 h of reaction (95%), thereby confirming that the coating with the manganese-supported TiO₂ resulted in a very efficient monolithic catalyst for ozone decomposition reaction. The activity of the manganese active sites was preserved after impregnation/dispersion of the Mn phase onto the alumina wash-coated cordierite honeycomb monolith. Then a 20 min purge with air was made, prior to introducing ethanol and ozone into the reactor, so as to perform the VOC oxidation with ozone over the 5Mn-Ti/FM monolith. Again, a very high ozone conversion could be reached (96% after 3 h of reaction), while simultaneously achieving an almost complete ethanol conversion (99%).

In the next step, the catalytic oxidation of ethanol using ozone was investigated over the full monolithic series (Ti/FM, 5Mn-Ti/FM and 0.5Pd-5Mn-Ti/FM) under dry and humid conditions. Results presented in Table 4 and Figure 8 indicated that ethanol was fully converted over the manganese and palladium-manganese monolithic catalysts (5Mn-Ti/FM and 0.5Pd-5Mn-Ti/FM). Very high ozone conversion values were obtained (93–96%), with selectivity to CO₂ ranging from 82 to 91%. No acetaldehyde was observed for the Pd-based monolithic catalyst, and CO was the only by-product detected. It is also worth mentioning that the Pd containing full monolith (with **54 channels**) exhibited a stable activity as a function of time on stream under both dry and humid air (Figure 8), as observed for the corresponding catalyst in powdered form (Figure 5). The monolith impregnated with the TiO₂mM support (Ti/FM) also proved to be active in the total oxidation of ethanol (>94% conversion and 72% CO₂ selectivity). However, the conversion of ozone was found to be low (~20%), thereby confirming that the doping elements (Mn and Pd) are required to ensure high ethanol and ozone conversions, along with high selectivity to CO₂. This is in agreement with what was previously observed with the TiO₂mM support in powdered form.

Table 4. Ethanol oxidation on the impregnated full monolithic catalysts (F_M) with **54 channels**, in dry and humid air (10% RH) conditions (total flow rate = 500 mL·min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C, Time = 3 h).

Catalyst	Ti/FM		5Mn–Ti/FM		0.5Pd–5Mn–Ti/FM	
Atm. (Air)	Dry	Humid	Dry	Humid	Dry	Humid
EtOH conversion (%)	96	94	99	99	100	100
CO ₂ selectivity (%)	72	71	82	83	89	91
CO selectivity (%)	22	19	17	16	11	9
ACA selectivity (%) ¹	6	10	1	1	0	0
O ₃ conversion (%)	24	17	96	93	95	94

¹ ACA = acetaldehyde.

The slight variations observed in the conversion and selectivity values within the 5Mn/TiO₂mM and 0.5Pd-5Mn/TiO₂mM-based monoliths do not establish a clear picture on the evolution of the performances for ethanol total oxidation with the composition of the catalysts, because ethanol was fully converted in all cases. In this respect, part of the FM monolith channels was plugged, so as to decrease the residence time to 0.03 s, along with the amount of impregnated active phase in contact with the gas flow. The resulting partially plugged monolithic catalysts (**PM** series) were composed of **16 channels** instead of **54 channels** (Table S2—ESI). The results are presented in Table 5 and Figure 9. The 0.5Pd-5Mn/TiO₂mM-based monoliths **PM** proved to be more efficient in ethanol oxidation than the corresponding 5Mn/TiO₂mM counterpart, with higher CO₂ selectivity.

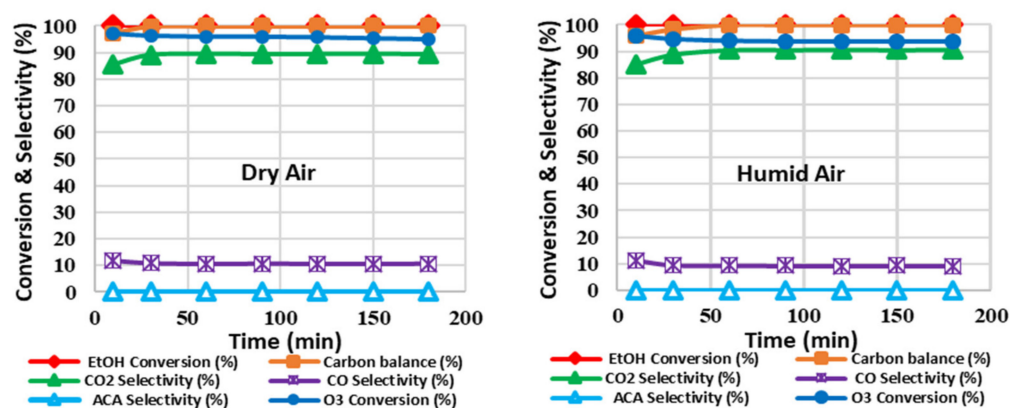


Figure 8. Ethanol conversion, ozone conversion, product selectivity and carbon balance as a function of time on stream in dry (left) and humid (right) conditions (residence time = 0.1 s, total flow rate = 500 mL·min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C) for the palladium-doped full monolithic catalyst with **54 channels** (0.5Pd–5Mn–Ti/FM).

Table 5. Ethanol oxidation on the impregnated partially plugged monolithic catalysts (PM) with **16 channels**, in dry and humid air (10% RH) conditions (total flow rate = 500 mL·min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C, Time = 3 h).

Catalyst	Ti/PM		5Mn–Ti/PM		0.5Pd–5Mn–Ti/PM	
	Atm. (Air)		Dry	Humid	Dry	Humid
EtOH conversion (%)			77	80	80	89
CO ₂ selectivity (%)			65	70	70	74
CO selectivity (%)			24	17	17	15
ACA selectivity (%) ¹			11	13	13	11
O ₃ conversion (%)			15	10	47	40

¹ ACA = acetaldehyde.

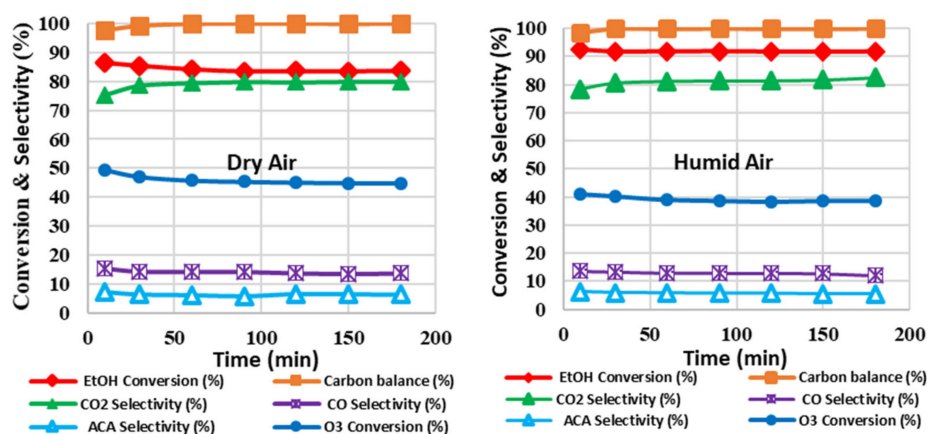


Figure 9. Ethanol conversion, ozone conversion, product selectivity and carbon balance as a function of time on stream in dry (left) and humid (right) conditions (total flow rate = 500 mL·min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C) for the palladium-doped partially plugged monolithic catalyst (FM) with **16 channels** (0.5Pd–5Mn–Ti/PM).

The presence of palladium was shown to significantly increase the conversion of ethanol to CO₂ by decreasing drastically the formation of acetaldehyde. Moreover, the enhanced effect of water vapor on the oxidation of ethanol using ozone was also noticed for all monolithic catalysts, as in the case of the catalysts in powdered form. The effect was more pronounced for the 0.5Pd–5Mn/TiO₂mM-based monolith. In the dry air stream,

80% or 84% of ethanol could be oxidized by O_3 over 5Mn–Ti/PM and 0.5Pd–5Mn–Ti/PM, respectively. In the humid air stream, 89% of the ethanol was converted by O_3 over 5Mn–Ti/PM, while 92% was oxidized over the Pd containing monolith, respectively. This corresponds to an increase of ca. 10% under humid conditions.

The beneficial effect of water vapor on the conversion of ethanol and selectivity to CO_2 can be explained by the extensive oxidation of the organic byproducts formed. Such a phenomenon was already reported by Einaga and Futamura in benzene oxidation using ozone over alumina-supported manganese oxides [41]. The authors showed that water vapor promoted the oxidation of the byproducts such as formic acid on the catalyst surface. They demonstrated by FTIR spectroscopy studies that the surface formates were not completely oxidized with ozone in the absence of water vapor, whereas their oxidation with ozone was promoted by the addition of water vapor. In our case, the selectivity to CO_2 was maximal in the presence of humid air, thereby confirming the beneficial role of water for complete oxidation. The positive effect of water was more visible for the partially plugged monolithic catalysts (PM series, Table 5) than for the full monoliths (FM series, Table 4), because the residence time was lower in this case (16 channels instead of 54 channels).

In addition to the catalytic performances (in terms of conversion and selectivity to CO_2), the level of residual ozone after the catalytic run is also of great concern. Highly efficient monolithic catalysts able to simultaneously achieve complete ethanol oxidation and ozone decomposition are desired. According to the European and French regulation rules [66], the residual concentration of ozone in indoor air should not exceed 60 ppb. By taking advantage of the full impregnated monoliths (54 channels) that have proven to be effective catalysts in oxidizing ethanol to CO_2 , we investigated the ability of two 0.5Pd–5Mn–Ti/FM monoliths in series to be used for ethanol removal from indoor air without any residual ozone. The catalytic oxidation reaction was performed under dry and humid air conditions using ozone. The results are presented in Table 6. These two 0.5Pd–5Mn–Ti/FM monoliths in series reached full ethanol conversion, while ensuring almost total selectivity to CO_2 (98% and 99% in dry and humid air stream, respectively). No formation of acetaldehyde was observed. Most importantly, the residual concentration of ozone was less than the detection limit (less than 10 ppb), thereby demonstrating that the proposed monolithic catalytic system can completely convert low concentrations of ethanol to CO_2 at low temperatures without residual O_3 being emitted. Likewise, complete ozone decomposition (below the detection limit) was observed in the absence of ethanol. By fulfilling the specifications required for onboard systems, these Pd–Mn/TiO₂-based monoliths can be envisaged for ethanol removal from indoor air, such as in vehicles and rooms, etc. These Pd–Mn/TiO₂ impregnated cordierite monoliths may fit with an industrial use. By extrapolation from the laboratory results for a residence time of 0.2 s, we estimated the size of an industrial reactor able to treat 1000 m³·h^{−1} of air at a volume of 56 L (ϕ = 30 cm, L = 80 cm) containing about 0.67 kg of catalyst. Such estimates are fully consistent with an industrial process, since VOC emission levels in indoor air (e.g., ethanol) are generally less than 1 ppm, which would need far less than 70 ppm of ozone to be oxidized and hence improve the process safety.

Table 6. Ethanol oxidation on two 0.5Pd–5Mn–Ti/FM full monolithic catalysts in series (54 channels) in dry and humid air (10% RH) conditions (total flow rate = 500 mL·min^{−1}, [EtOH] = 10 ppm, [O₃] = 70 ppm, T = 60 °C, Time = 3 h).

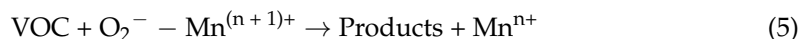
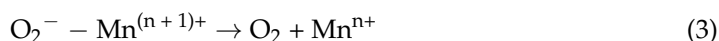
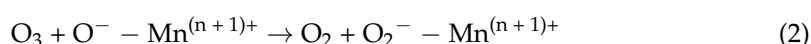
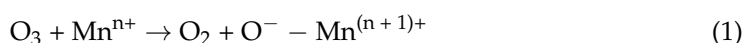
Catalysts	Two 0.5Pd–5Mn–Ti/FM in Series	
	Dry	Humid
EtOH conversion (%)	100	100
CO ₂ selectivity (%)	98	99
CO selectivity (%)	2	1
ACA selectivity (%) ¹	0	0
O ₃ conversion (%)	≈100 (<10 ppb)	≈100 (<10 ppb)

¹ ACA = acetaldehyde.

2.3. Active Species and Reaction Mechanism

The reaction of VOC oxidation using ozone follows the Langmuir–Hinshelwood (L–H) and/or Mars–Van Krevelen (MvK) mechanisms, depending on the nature of the catalyst, reactant composition and reaction conditions, as discussed in the review recently published by Liu et al. [39]. It is proposed that catalysts supported on inert materials like silica follow the L–H mechanism at low temperature, while catalysts with rich surface oxygen species, such as MnOx/Al₂O₃, follow the MvK mechanism. By using in situ DRIFT spectroscopy, Li et al. [67] found that toluene could be ultimately oxidized into CO₂ by reactive oxygen species (O^{2−}, O₂^{2−}, O[−]) generated from ozone decomposition over oxygen vacancies of MnO₂ at room temperature.

The mechanism of oxidation of VOCs using ozone (by ozone decomposition) on (supported) manganese oxide-based catalysts is based on the following equations. The first step is the reaction of ozone with a catalyst oxygen vacancy, leading to the formation of molecular oxygen and atomic oxygen O* adsorbed on the catalyst surface (Equation (1)). Then a second molecule of ozone reacts with the atomic oxygen to form a O₂* peroxy species and another O₂ molecule (Equation (2)). Next, the decomposition of the peroxide species leads to gas phase O₂ along with an oxygen vacancy on the catalyst (Equations (1) and (3)). Then, the volatile organic compound interacts with the reactive oxygen species (O[−] and O₂[−]) on the surface of the manganese-based catalyst to generate the oxidized products (Equations (4) and (5)) [43,68,69].



These reactions imply a redox mechanism between Mn³⁺ and ozone leading to the formation of Mn⁴⁺ and O[−] and O₂[−]. It is thus expected that such process would be favored by the presence of Mn³⁺ instead of Mn⁴⁺ (i.e., Mn₂O₃ instead of MnO₂). This hypothesis is supported by the results obtained in the present work. Among the whole Mn/TiO₂ series, the best performances were obtained with the lowest manganese content (5Mn/TiO₂mM-400, Table 2), which corresponds to the highest Mn³⁺/Mn⁴⁺ ratio. Additionally, we also checked that the ozone conversion does not vary significantly in the presence or absence of VOC, suggesting that ozone activation into reactive oxygen species (reactions 3 and 4) is the rate limiting step of the process.

The addition of a noble metal such as Ru or Ag to manganese-containing zeolite catalysts resulted in significantly enhanced performances in the oxidation of VOC using ozone [67]. It was attributed to a positive interaction between the noble metal and Mn. In another report, the addition of a small amount of Pd to a mesoporous MnOx–CeO₂ mixed oxide catalyst greatly improved the reduction of Mn oxides, as shown by the shift of the reduction peak from 270 °C to 190 °C [70]. Such a phenomenon can be explained by a hydrogen spillover effect. However, the authors noticed that the presence of Pd did not modify the mobility of oxygen species between the MnOx and CeO₂ oxides. Rezaei et al. [71] showed that the addition of platinum to a MnOx/Al₂O₃ catalyst enhanced the catalytic activity due to the interaction between Pt and the manganese oxide. As a result, a change in the electronic structure of Mn was observed through the formation of Mn–O–Pt bonds. By contrast, any improvement of the catalytic activity was observed with the palladium-doped MnOx/alumina sample, which was explained by a preferential Pd deposition on the alumina surface and lack of atomic interaction with manganese. Under our experimental conditions, a positive effect of Pd addition on the conversion of ethanol and selectivity to CO₂ was observed, which could result from a high dispersion of manganese oxide at

the surface of the TiO_2 support. Consequently, the presence of palladium should increase the ozone transformation on the catalysts by favoring electron transfer from Mn^{3+} to O_3 , thereby leading to O^- and Mn^{4+} .

3. Materials and Methods

3.1. Powder Catalysts Preparation

The hierarchical bimodal meso–macroporous TiO_2 support (TiO_2mM) was prepared in the presence of a single surfactant following a procedure adapted from Yuan et al. [72], though key modifications were made. A total of 10.42 g of cetyltrimethylammonium bromide (CTAB, >96%, Sigma-Aldrich, St. Quentin Fallavier Cedex, France) was dissolved in 94.3 g of deionized water to prepare a 10 wt% solution. The suspension was stirred at room temperature (RT) for about 3 h, before the addition, under stirring, of 25.12 mL (24.12 g) of titanium isopropoxide (97%, Sigma-Aldrich, St. Quentin Fallavier Cedex, France), using a syringe working with automatically controlled delivery of the liquid. The resulting sol was further matured under stirring for 1 h at RT. The obtained gel was then autoclaved under static conditions in a polypropylene bottle at 80 °C for 24 h. The resulting solid was recovered by centrifugation, then washed twice with deionized water and air-dried at 60 °C overnight before being calcined at 400 °C for 4 h.

Catalysts were prepared by successive wet impregnation of the TiO_2mM support by aqueous solutions of manganese nitrate with different (5–20) wt% of Mn. In a typical method (5 wt% Mn), a solution containing 0.9149 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, St. Quentin Fallavier Cedex, France) and 15 mL of deionized water, was prepared. The solution was stirred a few minutes until the salt was dissolved. Then, 3.8013 g of TiO_2mM support was dispersed in the solution under stirring at room temperature. The suspension was further stirred for one hour and subsequently poured in a flat crucible at 100 °C overnight. The resulting powder was calcined at 400 °C during 4 h with a heating rate of 1 °C·min^{−1}, under air flow (2 L·h^{−1}). The catalyst was referred to as 5Mn/ TiO_2mM , and the corresponding 10 wt% and 20 wt% of Mn as 10Mn/ TiO_2mM and 20Mn/ TiO_2mM , respectively. The manganese (5 wt%) impregnated titania catalysts were also calcined at 200 °C (5Mn/ TiO_2mM -200) for comparison purposes. The 5Mn/ TiO_2mM catalysts calcined at 400 °C were further impregnated with an aqueous 0.5 wt% Pd palladium nitrate solution. A solution containing 0.0128 g of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, St. Quentin Fallavier Cedex, France) and 3 mL of deionized water was prepared. The solution was stirred a few minutes until the salt was dissolved. Then, 0.9955 g of the calcined 5Mn/ TiO_2mM compound were dispersed in the Pd solution under stirring at room temperature. The suspension was further stirred for one hour and subsequently poured in a flat crucible overnight at 100 °C. The resulting powder was calcined at 400 °C for 4 h with a heating rate of 1 °C·min^{−1}, under air flow (2 L·h^{−1}). The palladium–manganese impregnated TiO_2 catalyst was labelled as 0.5Pd–5Mn/ TiO_2mM .

Table 1 shows the catalyst naming format, as well as the manganese and palladium content of the catalysts (target and experimental values).

3.2. Monolithic Catalysts Preparation

Cordierite honeycomb monoliths of cylindrical shape with a 15 mm diameter and 6 mm height were cut from larger monoliths (200 cpsi) wash-coated with 20 wt% of γ -alumina. These small monoliths were formed by about 54 channels of square sections of 1.6 mm of inner side, which represented about 20.7 cm² of surface area. Such cordierite monoliths containing 54 channels were labelled as FM (full monoliths).

Cordierite monolithic catalysts were prepared by a three-step procedure, consisting of (i) coating of alumina wash-coated monoliths in an aqueous suspension (241.5 g·L^{−1}) of TiO_2mM through a “dip and dry” technique followed by calcination and (ii) impregnation with a manganese nitrate solution (followed by calcination) and then (iii) with an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (followed by an additional calcination).

Wash-coated cordierite monoliths were calcined at 400 °C prior to the TiO₂ coating step and impregnation of the catalytically active components. The TiO₂ slurry was prepared by mixing the previously prepared TiO₂mM powder (5 g in 20 mL of distilled water) with 0.7 mL of concentrated nitric acid under stirring. The suspension was stirred overnight, before the monoliths were dip-coated with this milky homogeneous slurry. After drying at 120 °C for 1 h, the same wash-coating procedure was repeated until 14–15 wt% of TiO₂mM was deposited. The resulting monoliths (labelled as Ti-FM) were finally calcined at 400 °C for 4 h. Then impregnation of manganese oxide was carried out using a 0.05 mol L^{−1} manganese nitrate solution in which the TiO₂ coated-cordierite monolith (Ti-FM) was immersed for 2 h, then dried at 120 °C and further calcined at 400 °C for 4 h. This procedure was repeated until the amount of manganese was about 5 wt% (between 3 and 5 cycles of impregnation–calcination were needed). The resulting Mn-Ti/monolith was labelled as 5Mn-Ti/FM. The final step consisted in impregnating Pd by immersing the 5Mn-Ti/FM monolith in a palladium nitrate solution (0.5 wt% Pd), followed by the same drying and calcination processes as described above, yielding the 0.5Pd-5Mn-Ti/FM monolith.

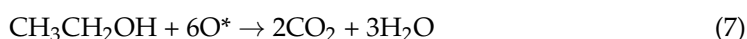
An analogous series of (Pd)-Mn/TiO₂mM monolithic catalysts was also prepared following the same impregnation–drying–calcination procedure as explained above, except that a large part of the **54 channels** was plugged with Araldite[®] glue, so as to keep only **16 channels** accessible to the gas flow. The corresponding partially plugged (**PM**) monolithic catalysts were referred to as Ti/**PM**, 5Mn-Ti/**PM** and 0.5Pd-5Mn-Ti/**PM**. Some characteristics of the FM and **PM** monolithic catalysts are shown in Table S1.

3.3. Characterization of Powder Catalysts

Powder X-ray diffraction (XRD) analyses were recorded with an EMPYREAN (Houston, TX, USA) diffractometer (Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$)) equipped with an X'celerator type detector with a 2° opening operating at 45 kV and 40 mA. The diffraction patterns were recorded in the 2θ value range of 20–80° (with a step size of 0.08° and a step time of 2 s). Nitrogen adsorption–desorption isotherms were measured on a TRISTAR 3000 (Fairfield, NJ, USA) gas adsorption apparatus at −196 °C. Prior to N₂ adsorption, the samples were degassed under secondary vacuum at 150 °C overnight. The specific surface area (SBET in m²·g^{−1}) was determined from the linear part (0–0.23 P/P₀) of the BET plot. The total pore volume was measured at P/P₀ equal to 0.99, and the mean pore diameter was determined by the BJH method applied to the desorption branch. The content of manganese and palladium was determined by ICP-OES using a Perkin Elmer Optima 2000DV analyzer (Waltham, MA, United States). Raman spectra were obtained using a Labram HR800UV HORIBA JOBIN YVON (Kyoto, Japan) Raman confocal microscope equipped with a Peltier-cooled CCD detector and an Ar laser (514.532 nm). The spectral resolution was 0.5 cm^{−1}. Temperature programmed reduction experiments (TPR) were performed on a Micromeritics AutoChem 2910 instrument. Samples were outgassed with helium at 300 °C for 1 h (30 mL min^{−1}) with a heating rate of 10 °C·min^{−1}, prior to heating under H₂ flow (5 vol% diluted in Ar, 50 mL·min^{−1}) from 20 to 800 °C (heating rate: 10 °C·min^{−1}).

3.4. Catalytic Oxidation

The catalytic oxidation of ethanol was carried out in a conventional flow reactor at atmospheric pressure at 60 °C using ozone. Ozone was generated by flowing pure oxygen through a non-thermal plasma reactor; the exiting ozone–oxygen mixture was then diluted by ethanol–air mixture from a Bronkhorst evaporating system. According to the reaction of ozone activation on the surface of a catalyst leading to one atomic oxygen O* (Equation (6)) and the total oxidation of ethanol into carbon dioxide and water (Equation (7)), six molecules of ozone (as O*) are required to convert one molecule of ethanol to CO₂.



Here, a slight stoichiometric excess of ozone was used with respect to the concentration required to fully oxidize ethanol to CO₂ and water. An O₃/EtOH molar ratio equal to 7 was used instead of the stoichiometric ratio of 6, so as not to be in default of oxidant during the catalytic oxidation. The resulting concentration of ozone and ethanol was fixed to 70 ppm and 10 ppm, respectively. For humid conditions, water was introduced in the gas flow by bubbling the air flow in a saturator-type vessel containing water prior to being mixed with an ethanol–air mixture. Here, a controlled air stream with desired low humidity conditions was used. The humidity was fixed to 10% of relative humidity (RH) at 25 °C, which corresponds to 3130 ppmv of water in the final gas flow.

In a first step, the tests were performed with 20 mg of catalyst in a powder form with a total flow rate of 500 mL·min^{−1} and a GHSV of 1.5 × 10⁶ mL·g^{−1}·h^{−1}. More details about the experimental setup and reaction procedure are available in the Scheme S1.

Calculations based on adiabatic conditions [73,74] in this reactor indicate that the increase of temperature was less than 1 °C for a complete ethanol conversion into CO₂%, thereby confirming that there is no significant increase of temperature at the catalyst surface under our experimental conditions.

The reaction products are CO₂, CO, acetaldehyde (CH₃CHO, labeled as ACA) and water. The quantification of gas products was performed by online gas chromatography (Varian 430-GC and Varian CP-4900 Micro GC, Palo Alto, CA, USA). Ozone was analyzed online by an ozone analyzer (Environnement S.A. type O3 42 M, Paris, France) based on the UV photometric method at 254 nm. The ethanol and ozone conversion, along with the product selectivity (CO₂, CO, acetaldehyde) and the carbon balance are as follows (Equations (8)–(13), respectively):

$$\text{Ethanol conversion : } X_{\text{Et-OH}} (\%) = 100 \cdot \frac{(\text{conc}_{\text{EtOH}_0} - \text{conc}_{\text{EtOH}_f})}{\text{conc}_{\text{EtOH}_0}} \quad (8)$$

$$\text{Ozone conversion : } X_{\text{O}_3} (\%) = 100 \cdot \frac{(\text{conc}_{\text{O}_3_0} - \text{conc}_{\text{O}_3_f})}{\text{conc}_{\text{O}_3_0}} \quad (9)$$

$$\text{CO}_2 \text{ selectivity : } S_{\text{CO}_2} (\%) = 100 \cdot \frac{\text{conc}_{\text{CO}_2}}{2 \cdot (\text{conc}_{\text{EtOH}_0} - \text{conc}_{\text{EtOH}_f})} \quad (10)$$

$$\text{CO Selectivity : } S_{\text{CO}} (\%) = 100 \cdot \frac{\text{conc}_{\text{CO}}}{2 \cdot (\text{conc}_{\text{EtOH}_0} - \text{conc}_{\text{EtOH}_f})} \quad (11)$$

$$\text{Acetaldehyde selectivity : } S_{\text{ACA}} (\%) = 100 \cdot \frac{\text{conc}_{\text{ACA}}}{(\text{conc}_{\text{EtOH}_0} - \text{conc}_{\text{EtOH}_f})} \quad (12)$$

$$\text{Carbon balance: CB (\%)} = S_{\text{ACA}} + S_{\text{CO}} + S_{\text{CO}_2} \quad (13)$$

Subscripts 0 and *f* refer to reactor inlet and outlet concentration, respectively, of ethanol and oxidized products.

4. Conclusions

The catalytic oxidation of ethanol from indoor air was studied at low temperature (60 °C) over a series of Mn/TiO₂ and Pd–Mn/TiO₂ catalysts in powdered and monolithic forms, under dry and humid air streams, using ozone as oxidant. The catalytic experiments were performed with a slight stoichiometric excess of ozone with respect to the concentration required to fully oxidize ethanol to CO₂ (70 ppm of ozone for 10 ppm of ethanol). Our study demonstrated that the Pd–Mn/TiO₂ catalyst was more efficient in oxidizing ethanol, while simultaneously increasing ozone decomposition, than the Mn/TiO₂ counterparts. Additionally, we have shown that the impregnation of the 0.5Pd–5Mn/TiO₂ sample on alumina pre-washcoated cordierite monoliths led to highly efficient catalysts in terms of ethanol conversion and selectivity to CO₂. Ethanol was fully oxidized with 99% CO₂ selectivity over two 0.5Pd–5Mn–Ti/FM monoliths in series, with a residual ozone concentration less than 10 ppb (at least 6 times lower than the more severe rules on maximum

ozone emissions in indoor rooms). Therefore, the proposed monolithic systems may be considered for indoor air treatment containing low concentrations of ethanol. In a next step, the low temperature ozone-enhanced oxidation of low concentration of other VOCs will be investigated over such monolithic catalysts.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal12020172/s1>, Scheme S1: Experimental setup and reaction procedure, Table S1: Textural properties of the TiO₂mM support and the corresponding supported Mn and Pd catalysts (all calcined at 400 °C), Table S2: Characteristics of the monolith catalysts (FM: full monolith = **54 channels**; PM: partially plugged monolith = **16 channels**), Figure S1: Raman spectra of the meso-macrostructured TiO₂mM support and the corresponding supported Mn/TiO₂mM 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, [O₃] = 70 ppm, T = 60 °C) for the 10Mn/TiO₂ 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, [O₃] = 70 ppm, T = 60 °C) for the 20Mn/TiO₂ 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** ([O₃] = 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, [O₃] = 70 ppm, T = 60 °C).

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