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 was 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

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 (NOx) and sulfur oxides (SOx) 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 MnOx [34], Mn3O4, MnO2, 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 MnOx 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 (MnOx) 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 MnOx 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/TiO2 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.

| Catalyst          | Mn (wt%)          | Pd (wt%)          | Calcination Temperature (°C) |
|-------------------|-------------------|-------------------|-----------------------------|
| TiO2mM            |                   |                   |                             |
| 5Mn/TiO2mM-400    | 5                 | 4.56              | -                           | 400                         |
| 5Mn/TiO2mM-300    | 5                 | 4.62              | -                           | 300                         |
| 5Mn/TiO2mM-200    | 5                 | 4.85              | -                           | 200                         |
| 10Mn/TiO2mM-400   | 10                | 9.74              | -                           | 400                         |
| 20Mn/TiO2mM-400   | 20                | 18.40             | -                           | 400                         |
| 0.5Pd–5Mn/TiO2mM  | 5                 | 1.71              | 0.5                         | 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 pyrrolusite MnO (JCPDS card 98-024-6888) and to bixbyte MnO2 (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 Mn₃O₄ (bixbyite) did not allow us to distinguish between either manganese oxide phases. Part of the XRD reflections of MnO₂ and Mn₃O₄ 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-macroporous TiO₂mM support and the corresponding supported Mn and Pd samples (all calcined at 400 °C). Bottom: JCPDS references MnO₂ and Mn₃O₄.

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 TiO₃mM and 5Mn/TiO₃mM samples to 5.6 nm for the sample with the highest Mn loading (20Mn/TiO₃mM). The specific surface areas and pore volumes of the parent meso–macrostructured titania and the corresponding Mn/TiO₃mM and Pd–Mn/TiO₃mM samples are summarized in Table S1 (ESI). The TiO₃mM 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/TiO₃mM (Figure 2) and Pd–Mn/TiO₃mM 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/TiO₃mM), in agreement with its concomitant decrease of surface area and mesopore size.

![Figure 2](image_url)

**Figure 2.** N₂ adsorption–desorption isotherms for the meso–macrostructured TiO₃mM support and the corresponding supported Mn/TiO₃mM samples (5, 10 and 20 Mn wt%).

Note that the macroporous part of the 0.5Pd–Mn/TiO₃mM 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/TiO₃mM 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/TiO₃mM sample (Figure S1—ESI). First, the characteristic peaks of the anatase phase of the TiO₃mM 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/TiO₃mM) 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/TiO₃mM compound with the one containing 10 wt% of Mn, slight changes could be
seen on the Raman spectrum of the 10Mn/TiO\textsubscript{2mM} sample. The absorption band located at 643 cm\textsuperscript{-1} became broader, and the band at 518 cm\textsuperscript{-1} also showed a shoulder around 535 cm\textsuperscript{-1}. These bands could correspond to the signature of manganese oxide of the β-MnO\textsubscript{2} variety. Additional absorption bands were also observed on the spectrum of the 20Mn/TiO\textsubscript{2mM} sample compared with the 5Mn/TiO\textsubscript{2mM} compound, possibly corresponding to two different MnO types. Vibration bands of the β-MnO\textsubscript{2} variety were seen at 535–538 cm\textsuperscript{-1}, 667 cm\textsuperscript{-1} and 762 cm\textsuperscript{-1} on the Raman spectrum of the 20Mn/TiO\textsubscript{2mM} sample [60,61]. The peak appearing at 578 cm\textsuperscript{-1} was due to the γ-MnO\textsubscript{2} variety and was observed for the sample with the highest manganese content (20Mn/TiO\textsubscript{2mM}) and possibly also for the 10Mn/TiO\textsubscript{2mM} sample to a lesser extent.

2.1.5. H\textsubscript{2}-TPR Analysis

Redox properties of catalysts are important factors affecting the oxidation activity. The oxidation and reduction behavior of the 5Mn/TiO\textsubscript{2mM} series calcined at different temperatures (200, 300 and 400 °C) was investigated by H\textsubscript{2}-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 MnO\textsubscript{x} phases present in the samples with the lowest Mn content (5 wt%).

![Figure 3. H\textsubscript{2}-TPR profiles of the 5Mn/TiO\textsubscript{2mM} samples calcined at various temperatures (200, 300 and 400 °C).](image)

There was a marked difference between the TPR profiles of each of the 5Mn/TiO\textsubscript{2mM} samples. The H\textsubscript{2} 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 MnO\textsubscript{2} to MnO\textsubscript{3} [62,63]. Then MnO\textsubscript{3} was reduced into MnO\textsubscript{4} (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 MnO\textsubscript{2} to MnO\textsubscript{3}/MnO\textsubscript{4} 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 (MnO\textsubscript{3} to MnO\textsubscript{2}), along with a similar shoulder as that observed for the sample calcined at the lowest temperature (MnO\textsubscript{2} 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 Mn₃O₄. 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 MnO₂ to Mn₃O₄, while the second signal originated from the reduction of MnO₂ to MnO. According to the H₂ uptake between 100 and 500 °C, the relative amount of Mn⁴⁺ and Mn³⁺ 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 Mn⁴⁺ in the sample calcined at the lowest temperature (200 °C). By contrast, the corresponding 5Mn/TiO₂mM calcined at 400 °C was mainly composed of Mn³⁺ (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.

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 Mn³⁺/Mn⁴⁺ ratio.

### Table 2. Relative amount in percent of MnO₂ and Mn₃O₄ in the Mn/TiO₂mM samples calcined at various temperatures.

| Sample            | Calcination Temperature (°C) | H₂ Consumption (cm³ H₂/g STP) | %MnO₂ (as % Mn⁴⁺) | %Mn₂O₃ (as % Mn³⁺) |
|-------------------|-------------------------------|-------------------------------|-------------------|-------------------|
| 5Mn/TiO₂mM-200    | 200                           | 20.6                          | 94                | 6                 |
| 5Mn/TiO₂mM-300    | 300                           | 14.1                          | 39                | 61                |
| 5Mn/TiO₂mM-400    | 400                           | 11.4                          | 14                | 86                |
| 10Mn/TiO₂mM-400   | 400                           | 28.9                          | 40                | 60                |
| 20Mn/TiO₂mM-400   | 400                           | 61.0                          | 51                | 49                |

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. (%) | CO₂ Selectivity (%) | CO Selectivity (%) | O₃ conv. (%) | ACA ¹ (%) |
|------------------|-------------|------------|----------------|---------------------|-------------------|--------------|-----------|
| TiO2mM           | 400         | dry        | 73             | 61                  | 6                 | 33           | 12        |
| 5Mn/TiO2mM       |             |            |                |                     |                   |              |           |
| 200              | dry         | 86         | 67             | 18                  | 15                | 53          |
| 5Mn/TiO2mM       |             | humid      | 90             | 73                  | 16                | 11          |
| 5Mn/TiO2mM       | 400         | dry        | 95             | 83                  | 9                 | 8           | 64        |
| 5Mn/TiO2mM       |             | humid      | 99             | 85                  | 13                | 2           | 65        |
| 10Mn/TiO2mM      | 400         | dry        | 97             | 86                  | 12                | 2           | 66        |
| 10Mn/TiO2mM      |             | humid      | 99             | 86                  | 12                | 2           | 69        |
| 20Mn/TiO2mM      |             | dry        | 100            | 87                  | 12                | 1           | 70        |
| 20Mn/TiO2mM      |             | humid      | 100            | 86                  | 13                | 1           | 71        |
| 0.5Pd–5Mn/TiO2mM | 400         | dry        | 98             | 83                  | 13                | 4           | 77        |
| 0.5Pd–5Mn/TiO2mM |             | 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.

![Dry Air](image1.png) ![Humid Air](image2.png)

**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
enhancement of selectivity to CO\(_2\)) the Ti\(\text{O}_\text{mM}\) support led to a very low conversion of ozone (12%).

By contrast, a larger increase in the catalytic performance was observed for all Mn/Ti\(\text{O}_\text{mM}\) 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 O\(_3\) 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 CO\(_2\) was also observed with respect to the parent Ti\(\text{O}_\text{mM}\) (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/Ti\(\text{O}_\text{mM}\) and 10Mn/Ti\(\text{O}_\text{mM}\) samples showed a slight increase in the conversion of ethanol and in the selectivity to CO\(_2\) 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 Mn\(\text{O}_\text{mM}/\text{Al}_\text{mM}\) 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 CO\(_2\) 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/Ti\(\text{O}_\text{mM}\) catalysts. Zhu et al. [65] also reported that a high ozone decomposition rate was observed over \(\alpha\)-Mn\(\text{O}_\text{mM}\) 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/Ti\(\text{O}_\text{mM}\) catalyst, is shown in Figure 4. The higher EtOH and O\(_3\) 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/Ti\(\text{O}_\text{mM}\) samples (Table 3). Such a catalyst was selected with respect to the samples with higher manganese content, because it converted ethanol to CO\(_2\) with virtually the same efficiency in terms of conversion and selectivity, under humid air than did the 10Mn/Ti\(\text{O}_\text{mM}\) and 20Mn/Ti\(\text{O}_\text{mM}\) catalysts.

As expected, addition of a small amounts of Pd led to an increased O\(_3\) efficiency (Table 3, Figure 5). A higher ozone conversion was observed for the catalyst containing palladium (0.5Pd–5Mn/Ti\(\text{O}_\text{mM}\)) 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.
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/TiOz·M catalyst and 0.5Pd–5Mn/TiOz·M 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/TiOz·M 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.

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% TiOz 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 TiOz 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 TiOzmM 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 TiOzmM support in powdered form.

Table 4. Ethanol oxidation on the impregnated full monolithic catalysts (Fm) 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   |
| CO2 selectivity (%) | 72   | 71        | 82              | 83      | 89  | 91    |
| CO selectivity (%) | 22   | 19        | 17              | 16      | 11  | 9     |
| ACA selectivity (%) | 6    | 10        | 1               | 1       | 0   | 0     |
| O3 conversion (%) | 24   | 17        | 96              | 93      | 95  | 94    |

1 ACA = acetaldehyde.

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).

The slight variations observed in the conversion and selectivity values within the 5Mn/TiOzmM and 0.5Pd–5Mn/TiOzmM-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.

Table 5. Ethanol oxidation on the impregnated partially plugged monolithic catalysts (PM) with 16 channels, in dry and humid (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 |
|----------|-------|-----------|-----------------|
|          | Dry   | Humid     | Dry            | Humid          | Dry  | Humid |
| EtOH conversion (%) | 77 | 80 | 80 | 89 | 84 | 92 |
| CO2 selectivity (%)  | 65 | 70 | 70 | 74 | 80 | 83 |
| CO selectivity (%)   | 24 | 17 | 17 | 15 | 14 | 12 |
| ACA selectivity (%) 1 | 11 | 13 | 13 | 11 | 6 | 5 |
| O3 conversion (%)    | 15 | 10 | 47 | 40 | 45 | 39 |

1 ACA = acetaldehyde.

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 O3 over 5Mn–Ti/PM and 0.5Pd–5Mn–Ti/PM, respectively. In the humid air stream, 89% of the ethanol was converted by O3 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.

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 beneficial effect of water vapor on the conversion of ethanol and selectivity to CO2 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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} at low temperatures without residual O\textsubscript{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/TiO\textsubscript{2}-based monoliths can be envisaged for ethanol removal from indoor air, such as in vehicles and rooms, etc. These Pd–Mn/TiO\textsubscript{2} 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 m\textsuperscript{3}h\textsuperscript{-1} of air at a volume of 56 L (ø = 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\textsuperscript{-1}, [EtOH] = 10 ppm, [O\textsubscript{3}] = 70 ppm, T = 60 °C, Time = 3 h).

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

\(^1\text{ACA = acetaldehyde.}\)

### 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 (O2-, O22-, O2−) 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* peroxo 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].

\[
\begin{align*}
O_3 + Mn^{n+} & \rightarrow O_2 + O^– + Mn^{(n+1)+} \\
O_3 + O^– + Mn^{(n+1)+} & \rightarrow O_2 + O_2^2– + Mn^{(n+1)+} \\
O_2^– & \rightarrow O_2 + Mn^{n+} \\
VOC + O^– & \rightarrow Products + Mn^{n+} \\
VOC + O_2^– & \rightarrow Products + Mn^{n+}
\end{align*}
\]

These reactions imply a redox mechanism between Mn3+ and ozone leading to the formation of Mn4+ and O2- and O3-. It is thus expected that such process would be favored by the presence of Mn3+ instead of Mn4+ (i.e., Mn3O4 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/TiOmM-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 TiO2 support. Consequently, the presence of palladium should increase the ozone transformation on the catalysts by favoring electron transfer from Mn3+ to O3, thereby leading to O2- and Mn4+. 
3. Materials and Methods

3.1. Powder Catalysts Preparation

The hierarchical bimodal meso–macroporous TiO$_2$: support (TiO$_2$mM) 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 isopropanoxide (97%, Sigma-Aldrich, 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$_2$mM 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 Mn(NO$_3$_)$_2$·4H$_2$O (Sigma-Aldrich) 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$_2$mM 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$_2$mM, and the corresponding 10 wt% and 20 wt% of Mn as 10Mn/TiO$_2$mM and 20Mn/TiO$_2$mM, respectively. The manganese (5 wt%) impregnated titania catalysts were also calcined at 200 °C (5Mn/TiO$_2$mM-200) for comparison purposes. The 5Mn/TiO$_2$mM 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 Pd(NO$_3$_)$_2$·2H$_2$O (Sigma-Aldrich) 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$_2$mM 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$_2$mM.

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 $\gamma$-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 cm$^2$ 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$_2$mM 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 Pd(NO$_3$_)$_2$ (followed by an additional calcination).

Wash-coated cordierite monoliths were calcined at 400 °C prior to the TiO$_2$ coating step and impregnation of the catalytically active components. The TiO$_2$ slurry was prepared by mixing the previously prepared TiO$_2$mM 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 TiOcmM 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/TiOcmM 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 Kα radiation (λ= 1.5418 Å)) 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 20 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 m²g⁻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 °Cmin⁻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.

\[
O_3 \rightarrow O_2 + O^* \tag{6}
\]

\[
\text{CH}_3	ext{CH}_2	ext{OH} + 6O^* \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \tag{7}
\]

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):

\[
\text{Ethanol conversion: } X_{\text{EtOH}}(\%) = \frac{c_{\text{EtOH}} - c_{\text{EtOH}_f}}{C_{\text{EtOH}_i}}
\]

(8)

\[
\text{Ozone conversion: } X_{\text{O}_3}(\%) = \frac{c_{\text{O}_3} - c_{\text{O}_3_f}}{C_{\text{O}_3_i}}
\]

(9)

\[
\text{CO₂ selectivity: } S_{\text{CO₂}}(\%) = \frac{con_{\text{CO₂}}}{2 \cdot (c_{\text{EtOH}} - c_{\text{EtOH}_f})}
\]

(10)

\[
\text{CO Selectivity: } S_{\text{CO}}(\%) = \frac{con_{\text{CO}}}{2 \cdot (c_{\text{EtOH}} - c_{\text{EtOH}_f})}
\]

(11)

\[
\text{Acetaldehyde selectivity: } S_{\text{ACA}}(\%) = \frac{con_{\text{ACA}}}{(c_{\text{EtOH}} - c_{\text{EtOH}_f})}
\]

(12)

Carbon balance: CB (%) = S_{\text{ACA}} + S_{\text{CO}} + S_{\text{CO₂}}

(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.
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 www.mdpi.com/article/10.3390/catal12020172/s1, Scheme S1: Experimental setup and reaction procedure, Table S1: Textural properties of the TiO$_2$mM 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–macro-structured TiO$_2$mM 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).

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**References**

1. Liang, Q.; Bao, X.; Sun, Q.; Zhang, Q.; Zou, X.; Huang, C.; Shen, C.; Chu, Y. Imaging VOC distribution in cities and tracing VOC emission sources with a novel mobile proton transfer reaction mass spectrometer. *Environ. Pollut.* 2020, 265, 114628, https://doi.org/10.1016/j.envpol.2020.114628.

2. Zabiegała, B. Organic Compounds in Indoor Environments. *Pol. J. Environ. Stud.* 2006, 15, 383–393.

3. Wang, S.; Ang, H.M.; Tade, M.O. Volatile organic compounds in indoor environment and photocatalytic oxidation: State of the art. *Environ. Int.* 2007, 33, 694–705, https://doi.org/10.1016/j.envint.2007.02.011.

4. Edwards, R.D.; Jurvelin, J.; Koistinen, K.; Saarela, K.; Jantunen, M. VOC source identification from personal and residential indoor, outdoor and workplace microenvironment samples in EXPOLIS-Helsinki, Finland. *Atmos. Chem. Environ.* 2001, 35, 4829–4841, https://doi.org/10.1021/S1352-2310(01)00271-0.

5. Mayrhofer, S.; Mikoviny, T.; Waldburger, S.; Wagner, A.; Innerebner, G.; Franke-Whi, I.; MäRK, T.; Hansel, A.; Insam, H. Microbial community related to volatile organic compound (VOC) emission in household biowaste. *Environ. Microbiol.* 2006, 8, 1960–1974, https://doi.org/10.1111/j.1462-2920.2006.0076.x.

6. Schleibinger, H.; Laussmann, D.; Bornemah, C.-G.; Eis, D.; Rueden, H. Microbial volatile organic compounds in the air of moldy and mold-free indoor environments. *Indoor Air* 2008, 18, 113–124, https://doi.org/10.1111/j.1600-0668.2007.00513.x.

7. Atkinson, R. Atmospheric chemistry of VOCs and NOx. *Atmos. Environ.* 2000, 34, 2063–2101, https://doi-org/10.1016/S1352-2310(99)00460-4.

8. Simon, V.; Dumergues, L.; Ponche, J.-L.; Torres, L. The biogenic volatile organic compounds emission inventory in France: Application to plant ecosystems in the Berre-Marseilles area (France). *Sci. Total. Environ.* 2006, 372, 164–182, https://doi.org/10.1016/j.scitotenv.2006.08.019.
9. Virtanen, A.; Joutsensaari, J.; Koop, T.; Kannosto, J.; Yli-Pirilä, P.; Leskinen, J.; Mäkelä, J.M.; Holopainen, J.; Pöschl, U.; Kulmala, M.; Worsnop, D.; Laaksonen, A. An amorphous solid state of biogenic secondary organic aerosol particles. *Nature* **2010**, *467*, 824–827, https://doi.org/10.1038/nature09455.

10. Cicolella, A. Volatile Organic Compounds (VOC): Definition, classification and properties. *Rev. Mal. Respir.* **2008**, *25*, 155–163, https://doi.org/10.1016/s0761-8425(08)71513-4.

11. Jimoda, L.A. Effects of particulate matter on human health, the ecosystem, climate and materials: A review. *Facta Univ. Ser. Work. Living Environ. Prot.* **2012**, *9*, 27–44.

12. Heymes, F.; Manno Demoustier, P.; Charbit, F.; Fanlo, J.-L.; Moulin, P. Treatment of gas containing hydrophobic VOCs by a hybrid absorption– pervaporation process: The case of toluene. *Chem. Eng. Sci.* **2007**, *62*, 2576–2589, https://doi.org/10.1016/j.ces.2007.02.001.

13. Burg, P.; Fydruch, P.; Bimer, J.; Salbut, P.D.; Jankowska, A. Comparison of three active carbons using LSER modeling: Prediction of their selectivity towards pairs of volatile organic compounds (VOCs). *Carbon* **2002**, *40*, 73–80, http://dx.doi.org/10.1016/S0008-6223(01)00076-8.

14. Khan, F.I.; Ghoshal, A.K. Removal of volatile organic compounds from polluted air. *J. Loss Prevention Proc. Ind.* **2000**, *13*, 527–545, http://dx.doi.org/10.1016/S0950-4220(00)00007-3.

15. Biard, P.-F.; Couvert, A.; Renner, C.; Levasseur, J.-P. Intensification of volatile organic compounds mass transfer in a compact scrubber using the O/H:O advanced oxidation process: Kinetic study and hydroxyl radical tracking. *Chemosphere* **2011**, *85*, 1122–1129, https://doi.org/10.1016/j.chemosphere.2011.07.050.

16. Zhu, L.; Shen, D.; Luo, K.H. A critical review on VOCs adsorption by different porous materials: Species, mechanisms and modification methods. *J. Hazard. Mater.* **2020**, *389*, 122102, https://doi.org/10.1016/j.jhazmat.2020.122102.

17. Ceillier, C.; Ruaux, V.; Labousse, C.; Grange, P.; Gaigneaux, E. Extent of the participation of lattice oxygen from γ-MnO in VOCs total oxidation: Influence of the VOCs nature. *Catal. Today* **2006**, *117*, 350–355, https://doi.org/10.1016/j.cattod.2006.05.033.

18. Sekine, Y. Oxidative decomposition of formaldehyde by metal oxides at room temperature. *Atmos. Environ.* **2002**, *36*, 5543–5547, https://doi.org/10.1016/S1352-2310(02)00670-2.

19. Heck, R.M.; Farrauto, R.J. Automobile exhaust catalysts. *Appl. Catal A General* **2001**, *221*, 443–457, https://doi.org/10.1016/S0926-860X(01)00815-3.

20. Matsumoto, S. Recent advances in automobile exhaust catalysts. *Catal. Today* **2004**, *90*, 183–190, https://doi.org/10.1016/j.cattod.2004.04.048.

21. Kummer, J.T. Use of noble metals in automobile exhaust catalysts. *J. Phys. Chem.* **1986**, *90*, 4747–4752, https://doi.org/10.1021/j100141a008.

22. Gandhi, H.; Graham, G.W.; McCabe, R.W. Automotive exhaust catalysis. *J. Catal.* **2003**, *216*, 433–442, https://doi.org/10.1016/S0021-9517(02)00672-2.

23. Damyanova, S.; Bueno, J.M. Effect of CeO2 loading on the surface and catalytic behaviors of CeO2-Al2O3-supported Pt catalysts. *Appl. Catal A General* **2003**, *253*, 135–150, https://doi.org/10.1016/S0926-860X(03)00500-3.

24. Guisnet, M.; Dégé, P.; Magnoux, P. Catalytic oxidation of volatile organic compounds 1. Oxidation of xylene over a 0.2 wt% Pd/HFAU(17) catalyst. *Appl. Catal. B Environ.* **1999**, *20*, 1–13, https://doi.org/10.1016/S0926-3337(98)00087-3.

25. O’Malley, A.; Hodnett, B. K. The influence of volatile organic compound structure on conditions required for total oxidation. *Catal. Today* **1999**, *54*, 31–38, https://doi.org/10.1016/S0920-9861(99)00166-2.

26. Hubbard, C.P.; Otto, K.; Gandhi, H.S.; Ng, K.Y.S. Effects of support material and sulfation on propane oxidation activity over platinum. *J. Catal.* **1993**, *134*, 484–494, https://doi.org/10.1016/j.jcat.1993.1348.

27. Papaefthymiou, P.; Joanides, T.; Verykios, X.E. Performance of doped Pt/TiO2 (W++) catalysts for combustion of volatile organic compounds (VOCs). *Appl. Catal. B Environ.* **1998**, *15*, 75–92, https://doi.org/10.1016/S0926-3373(97)00038-6.

28. Ibrahim, M.; Labaki, M.; Giraudon, J.-M.; Lamonier, J.-F. Hydroxyapatite, a multifunctional material for air, water and soil pollution control: A review. *J. Hazard. Mater.* **2020**, *383*, 121139, https://doi.org/10.1016/j.jhazmat.2019.121139.

29. Rochard, G.; Olivet, L.; Tannous, M.; Poupin, C.; Siffert, S.; Cousin, R. Recent advances in the catalytic treatment of volatile organic compounds: A review based on the mixture effect. *Catalysts* **2021**, *11*, 1218, https://doi.org/10.3390/catal11101218.

30. Valange, S.; Vedrine, J.C. General and Prospective Views on Oxidation Reactions in Heterogeneous Catalysis. *Catalysts* **2018**, *8*, 483–503, https://doi.org/10.3390/catal8100483.

31. Hoffmann, M.R.; Martin, S.T.; Choi, W.; Bahnemann, D.W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96, https://doi.org/10.1021/cr00033a004.

32. Tidahy, H.L.; Siffert, S.; Wyrwalski, F.; Lamonier, J.-F.; Aboukais, A. Catalytic activity of copper and palladium based catalysts for toluene total oxidation. *Catal. Today* **2007**, *119*, 317–320, https://doi.org/10.1016/j.cattod.2006.08.023.

33. Zhang, S.; Guo, Y. Effects of large CuO contents on the performance of Pd/Al2O3-CuO catalysts in ethanol oxidation reaction. *Chem. Phys. Lett.* **2019**, *722*, 26–31, https://doi.org/10.1016/j.cplett.2019.03.003.

34. Bai, B.; Li, J.; Hao, J. 1D-MnO2, 2D-MnO and 3D-MnO for low-temperature oxidation of ethanol. *Appl. Catal. B Environ.* **2015**, *164*, 241–250, https://doi.org/10.1016/j.apcatb.2014.08.044.

35. Chen, S.; Li, H.; Hao, Y.; Chen, R.; Chen, T. Porous Mn-based oxides for complete ethanol and toluene catalytic oxidation: The relationship between structure and performance. *Catal. Sci. Technol.* **2020**, *10*, 1941–1951, https://doi.org/10.1039/C9CY02522G.

36. Wang, H.C.; Chang, S.H.; Hung, P.C.; Hwang, J.F.; Chang, M.B. Synergistic effect of transition metal oxides and ozone on PCDD/F destruction. *J. Hazard. Mater.* **2009**, *164*, 1452–1459, https://doi.org/10.1016/j.jhazmat.2008.09.093.
37. Wang, H.C.; Liang, H.S.; Chang, M.B. Chlorobenzene oxidation using ozone over ironoxide and manganese oxide catalysts. J. Hazard. Mater. 2011, 186, 1781–1787, https://doi.org/10.1016/j.jhazmat.2010.12.070.
38. Xiao, H.; Wu, J.; Wang, X.; Wang, J.; Mo, S.; Fu, M.; Chen, L.; Ye, D. Ozone-enhanced deep catalytic oxidation of toluene over a platinum-ceria-supported BEA zeolite catalyst. Mol. Catal. 2018, 460, 7–15, https://doi.org/10.1016/j.mcat.2018.09.005.
39. Liu, B.; Ji, J.; Zhang, B.; Huang, W.; Gan, Y.; Leung, D.Y.C. Catalytic ozonation of VOCs at low temperature: A comprehensive review. J. Hazard. Mater. 2022, 422, 126847, https://doi.org/10.1016/j.jhazmat.2021.126847.
40. Li, M.; Hui, K.N.; Hui, K.S.; Lee, S.K.; Cho, Y.R.; Lee, H.; Zhou, W.; Cho, S.; Chao, C.Y.H.; Li, Y. Influence of modification method and transition metal type on the physicochemical properties of MCM-41 catalysts and their performances in the catalytic ozonation of toluene. Appl. Catal. B Environ. 2011, 107, 245–252, https://doi.org/10.1016/j.apcatb.2011.07.018.
41. Einaga, H.; Futamura, S. Effect of water vapor on catalytic oxidation of benzene with ozone on alumina-supported manganese oxides. J. Catal. 2006, 243, 446–450, https://doi.org/10.1016/j.jcat.2006.07.021.
42. Dhandapani, B.; Oyama, S.T. Gas phase ozone decomposition catalysts. Appl. Catal. B Environ. 1997, 11, 129–166, https://doi.org/10.1016/S0167-1318(97)00044-6.
43. Reed, C.; Xi, Y.; Oyama, S. Distinguishing between reaction intermediates and spectators: A kinetic study of acetone oxidation using ozone on a silica-supported manganese oxide catalyst. J. Catal. 2005, 235, 378–392, https://doi.org/10.1016/j.jcat.2005.08.014.
44. Zhao, D.-Z.; Shi, C.; Li, X.-S.; Zhu, A.-M.; Jang, B.W.-L. Enhanced effect of water vapor on complete oxidation of formaldehyde in air with ozone over MnOx catalysts at room temperature. J. Hazard. Mater. 2012, 239–240, 362–369, https://doi.org/10.1016/j.jhazmat.2012.09.009.
45. Xi, Y.; Reed, C.; Lee, Y.-K.; Oyama, S.T. Acetone oxidation using ozone on manganese oxide catalysts. J. Phys. Chem. B 2005, 109, 17587–17596, https://doi.org/10.1021/jp052930g.
46. Reed, C.; Lee, Y.-K.; Oyama, S.T. Structure and oxidation state of silica-supported manganese oxide catalysts and reactivity for acetone oxidation with ozone. J. Phys. Chem. B 2006, 110, 4207–4216, https://doi.org/10.1021/jp054288w.
47. Einaga, H.; Futamura, S. Comparative study on the catalytic activities of alumina-supported metal oxides for oxidation of benzene and cyclobexane with ozone. React. Kinet. Catal. Lett. 2004, 81, 121–128, https://doi.org/10.1023/B:REAC.0000016525.91158.c5.
48. Einaga, H.; Futamura, S. Oxidation behavior of cyclobexane on alumina-supported manganese oxides with ozone. Appl. Catal. B Environ. 2005, 60, 49–55, https://doi.org/10.1016/j.apcatb.2005.02.017.
49. Einaga, H.; Futamura, S. Catalytic oxidation of benzene with ozone over alumina-supported manganese oxides. J. Catal. 2004, 227, 304–312, https://doi.org/10.1016/j.jcat.2004.07.029.
50. Einaga, H.; Futamura, S. Catalytic oxidation of benzene with ozone over Mn ion-exchanged zeolites. Catal. Commun. 2007, 8, 557–560, https://doi.org/10.1016/j.catcom.2006.07.024.
51. Einaga, H.; Teraoka, Y.; Ogata, A. Benzene oxidation with ozone over manganese oxide supported on zeolite catalysts. Catal. Today 2011, 164, 571–574, https://doi.org/10.1016/j.cat tod.2010.10.067.
52. Sugasawa, M.; Ogata, A. Effect of Different Combinations of Metal and Zeolite on Ozone-Assisted Catalysis for Toluene Removal. Ozone Sci. Eng. 2011, 33, 158–160, https://doi.org/10.1080/01999512.2010.547431.
53. Park, E.; Chin, S.; Kim, J.; Bae, G.-N.; Jurrj. Preparation of MnOx/TiOx ultrathin nanocomposite with large surface area and its enhanced toluene oxidation at low temperature. Powder Technol. 2011, 208, 740–743, https://doi.org/10.1016/j.powtec.2011.01.001.
54. Rezaei, A.; Soltan, J. Low temperature oxidation of toluene by ozone over MnOx/γ-alumina and MnOx/MCM-41 catalysts. Chem. Eng. J. 2012, 198–199, 482–490, https://doi.org/10.1016/j.cej.2012.06.016.
55. Chen, G.; Wang, Z.; Lin, F.; Zhang, Z.; Yu, H.; Yan, B.; Wang, Z. Comparative investigation on catalytic ozonation of VOCs in different types over supported MnOx catalysts. J. Hazard. Mater. 2020, 391, 122218, https://doi.org/10.1016/j.jhazmat.2020.122218.
56. Li, W.; Oyama, S.T. Ethanol oxidation using ozone over supported manganese oxide catalysts: An in situ laser Raman study. Stud. Surf. Sci. Catal. 1997, 110, 873–882, https://doi.org/10.1016/S0167-2991(97)81050-6.
57. Oyama, S.T.; Li, W.; Zhang, W. A Comparative study of ethanol oxidation with ozone on supported molybdenum and manganese oxide catalysts. Stud. Surf. Sci. Catal. 1999, 121, 105–110, https://doi.org/10.1016/S0167-2991(99)80052-4.
58. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physosorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure Appl. Chem. 2015, 87, 1051–1069, https://doi.org/10.1515/pac-2014-1117.
59. Hearne, G.R.; Zhao, J.; Dawe, A.M.; Pschedda, V.; Maaza, M.; Nieuwoudt, M.K.; Kibosamba, P. Effect of grain size on structural transitions in anatase TiO2: A Raman spectroscopy study at high pressure. Phys. Rev. 2004, 70, 134102–134103, https://doi.org/10.1103/PhysRevB.70.134102.
60. Julien, C.; Massot, M.; Rangan, S.; Lemal, M.; Guyomard., D. Study of structural defects in γ-MnOx by Raman spectroscopy. J. Raman Spectrosc. 2002, 33, 223–228, https://doi.org/10.1002/jrs.838.
61. Julien, C.; Massot, M.; Poinssignon, C. Lattice vibrations of manganese oxides: Part I. Periodic structures. Spectrochim Acta Part A 2004, 60, 689–700, https://doi.org/10.1016/S1386-1425(03)00279-8.
62. Kapteijn, F.; Vanlangeveld, A.D.; Moulijn, J.A.; Andreini, A.; Vuurman, M.A.; Turek, A.M.; Jehng, J.M.; Wachs, I.E. Alumina-supported manganese oxide catalysts: I. Characterization: Effect of precursor and loading. J. Catal. 1994, 150, 94–104, https://doi.org/10.1006/jcat.1994.1325.
63. Arena, F.; Torre, T.; Raimondo, C.; Parmaliana, A. Structure and redox properties of bulk and supported manganese oxide catalysts. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1911–1917, https://doi.org/10.1039/B100091H.

64. Ren, K.; Song, J.; Song, Y.-H.; Wang, H.; Liu, Z.; Liu, Z.-T.; Jiang, J.; Liu, Z.-W. Catalytic behavior of manganese oxides for oxidative dehydrogenation of ethylbenzene with carbon dioxide. *J. CO₂ Util.* **2017**, *22*, 63–70, https://doi.org/10.1016/j.jcou.2017.09.011.

65. Zhu, G.; Zhu, J.; Jiang, W.; Zhang, Z.; Wang, J.; Zhu, Y.; Zhang, Q. Surface oxygen vacancy induced α-MnOx nanofiber for highly efficient ozone elimination. *Appl. Catal. B Environ.* **2017**, *209*, 729–737. http://dx.doi.org/10.1016/j.apcatb.2017.02.068.

66. French Décret n° 2010-1250, Décret n° 2010-1250 du 21 octobre 2010 relatif à la qualité de l’air. *J. Off. République Française* **2010**, 96 pp.

67. Li, J.; Na, H.; Zeng, X.; Zhu, T.; Liu, Z. In situ DRIFTS investigation for the oxidation of toluene by ozone over Mn/HZSM-5, Ag/HZSM-5 and Mn-Ag/HZSM-5 catalysts. *Appl. Surf. Sci.* **2014**, *311*, 690–696, https://doi.org/10.1016/j.apsusc.2014.05.138.

68. Li, W.; Gibbs, G.V.; Oyama, S.T. Mechanism of ozone decomposition on a manganese oxide catalyst. 1. In situ Raman spectroscopy and ab initio molecular orbital calculations. *J. Am. Chem. Soc.* **1998**, *120*, 9041–9046, https://doi.org/10.1021/ja981441+.

69. Radhakrishnan, R.; Oyama, S.T. Ozone decomposition over manganese oxide Supported on ZrO2 and TiO2: A kinetic study using in situ laser Raman spectroscopy. *J. Catal.* **2001**, *199*, 282–290, https://doi.org/10.1006/jcat.2001.3167.

70. Zou, Z.Q.; Meng, M.; Zha, Y.Q. Surfactant-Assisted Synthesis, Characterizations, and Catalytic Oxidation Mechanisms of the Mesoporous MnOx–CeO2 and Pd/MnOx–CeO2 Catalysts Used for CO and C3H8 Oxidation. *J. Phys. Chem. C* **2010**, *114*, 468–477, https://doi.org/10.1021/jp908721a.

71. Rezaei, E.; Soltan, J.; Chen, N.; Lin, J. Effect of noble metals on activity of MnOx/γ-alumina catalyst in catalytic ozonation of toluene. *Chem. Eng. J.* **2013**, *214*, 219–228, https://doi.org/10.1016/j.cej.2012.10.044.

72. Yuan, Z.-Y.; Ren, T.-Z.; Vantomme, A.; Su, B.-L. Facile and generalized preparation of hierarchically mesoporous–macroporous binary metal oxide materials. *Chem. Mater.* **2004**, *16*, 5096–5106, https://doi.org/10.1021/cm0494812.

73. Bares, J.; Cerny, C.; Fried, V.; Pick, J. *Problems in Physical Chemistry*; Pergamon Press: Oxford, UK, 1961; p. 110.

74. Stull, D.; Westrum, F.; Sinke, C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley and Sons, Inc., 1969.