

Article

Gliding Arc Plasma Synthesis of MnO₂ Nanomaterials for Catalytic Oxidation of Benzene: Effect of Plasmagenic Gas

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Abstract: MnO₂ nanostructures were successfully synthesized via the reduction of KMnO₄ solutions using the gliding arc plasma (Plasma Glidarc) approach. Here, we highlight the effect of different plasmagenic gases, such as moist air (atmospheric air), dry air, nitrogen (N₂) or oxygen (O₂). The obtained materials were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), nitrogen physisorption and scanning electron microscopy (SEM). The crystalline structures of obtained MnO₂ polymorphs are mainly γ-MnO₂ and α-MnO₂, regardless of the feeding gas. The main reactive species, in addition to nitrogenous species like NO· radical generated with moist air, dry air or N₂ gas, other oxygenated species such as H₂O₂ (E°(O₂/H₂O₂) = 0.69 V) are produced with O₂ able to reduce KMnO₄ solution (E°(KMnO₄/MnO₂) = 1.70 V). Helium gas did not allow for the plasma reduction of the KMnO₄ solution, even after 60 min of exposure. Furthermore, gas humidification did not significantly affect the precipitation time or the properties of plasma-synthesized MnO₂. Atmospheric humidified air appears to be the best plasmagenic gas, as it allows for a shorter synthesis time and leads to a large specific surface area. All plasma-synthesized MnO₂ showed good activity during the catalytic oxidation of benzene. The use of different MnO₂ polymorphs (α-, δ- and γ-MnO₂) showed that, in addition to the specific surface area, the crystalline structure significantly affects the catalytic oxidation of benzene. K⁺ species inserted within the MnO₂ structure allow for their stability during the catalytic process. This work highlights the possibility to use different plasmagenic gases to prepare MnO₂ nanostructures through plasma glidarc for the catalytic oxidation of benzene.

Keywords: plasma glidarc; plasma reduction; MnO₂ nanostructured; plasmagenic gas; heterogeneous catalysis; benzene; catalytic oxidation



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1. Introduction

Tailoring the size, structure, texture and morphology during the synthesis of transition-metal oxides is a constant challenge for researchers [1]. Among the targeted oxides, MnO₂ appears affordable, environmentally friendly, and has various applications in energy storage [2] and catalysis [3–7]. Several synthesis methods, such as sol–gel, co-precipitation, thermal decomposition, hydrothermal and plasma processes, have been used to prepare MnO₂ nanostructures [1–4]. Knowing that the physical and chemical properties of obtained

MnO₂ affecting its applications such as environmental catalysis highly depend on the synthesis approach, gliding arc plasma (Plasma glidar) appears to be an effective route [1,8,9]. However, the effectiveness of plasma depends on the chosen voltage [8], gas flow [8], and plasmagenic gas, which directly impact the exposure time and the nature of the generated species. Du et al. reported that the nature of “plasmagenic” gas (N₂, O₂, air or argon) used in the gliding arc plasma route significantly affects the concentration of generated species (HO·, H₂O₂, O₃ and NO₃[−]), the pH and the conductivity of the reaction medium [10]. Indarto et al. showed that, while working with N₂ (compared to air and O₂), the plasma method had lower energy consumption [11]. Yu et al. observed that plasmagenic gas can affect the color, voltage and current of the gliding arc plasma discharge. They also recorded different degradation rates of naphthalene when changing the working gas during plasma synthesis (O₂ (92%) > air (80%) > N₂ (68%) > argon (24%)) and attributed the higher efficiency of O₂ to the HO· and O· radicals it generates [12]. On this basis, the plasmagenic gas used in gliding arc plasma as a synthesis route could qualitatively and quantitatively affect the species generated and consequently change the precipitation kinetic and physico-chemical properties of the obtained material. According to our knowledge, the effect of plasmagenic gas on the gliding arc plasma synthesis of metal oxide nanomaterials has not been explored systematically.

In this work, we explore the impact of plasmagenic gas on the plasma reduction time of Mn⁷⁺ solution and the possibility of preparing various polymorphs of MnO₂. Therefore, the KMnO₄ solution was exposed to gliding arc plasma discharge with air, dry air, N₂, O₂ or He as plasmagenic gas, with and without humidification. The products obtained were characterized through various physicochemical analyses, including XRD, FTIR, XPS, N₂ physisorption and SEM. The heterogeneous catalytic treatment of benzene and its derivative molecules appears as an alternative to thermal treatment, which generates harmful compounds, which are very toxic, carcinogenic, and persistent organic pollutants in the environment [5,13–18]. Their catalytic activities were measured during the degradation of benzene as an air model pollutant. We should be able to determine the best working gas based on the synthesis time and physicochemical characteristics, as well as the performance of the obtained materials as catalysts.

2. Results and Discussion

2.1. Effect of Plasmagenic Gas on the Precipitation Time and pH Solution

Figure 1 shows pre- and post-exposure images of KMnO₄ solution obtained from gliding arc plasma with moist air, dry air, N₂, O₂ or helium as plasmagenic gas. Except helium, the four other gases allowed for the plasma precipitation of KMnO₄ to black precipitates. The literature on the reducing species responsible for the plasma reduction of KMnO₄ solution with or without humidification of different gases is presented in Table 1 [10,12,19–22]. In the cases of moist air, dry air or N₂ gas, NO· species are responsible for the plasma reduction/precipitation of KMnO₄ solution. Except for N₂ gas without humidification, which produces NO· species only outside of the plasma plume, moist-air and dry-air gas without humidification produces NO· species in situ (that is inside) and outside the gliding arc plasma plume. With N₂ as the plasmagenic gas, N· radicals generated in situ react with H₂O at the surface of the solution to produce NO· radicals. However, as no nitrogen is present in the system while using O₂ gas, it is noteworthy that a precipitate formed with or without gas humidification. As the pH decreases, the reducing agent is most likely H₂O₂ ($E^\circ(\text{O}_2/\text{H}_2\text{O}_2) = 0.69 \text{ V}$) [23,24]. Nicol reported that H₂O₂ is oxidized to O₂ by reducing KMnO₄ solution in an acidic medium [25]. Dussault also showed that under a strongly acidic medium, H₂O₂ can be decomposed to oxygen molecules via the oxidation process [26]. Dry air allows for the in situ production of

$\text{NO}\cdot$ radicals through the recombination of $\text{N}\cdot$ and $\text{O}\cdot$ radicals. Additionally, as shown in Figure 1, the color of the gliding arc plasma plume varies with the type of plasmagenic gas used. Yu et al. also observed the same change [12]. However, the depletion of humidification has no noticeable effect on the plasma plume color (Figure S1), implying that the species generated are unaffected.

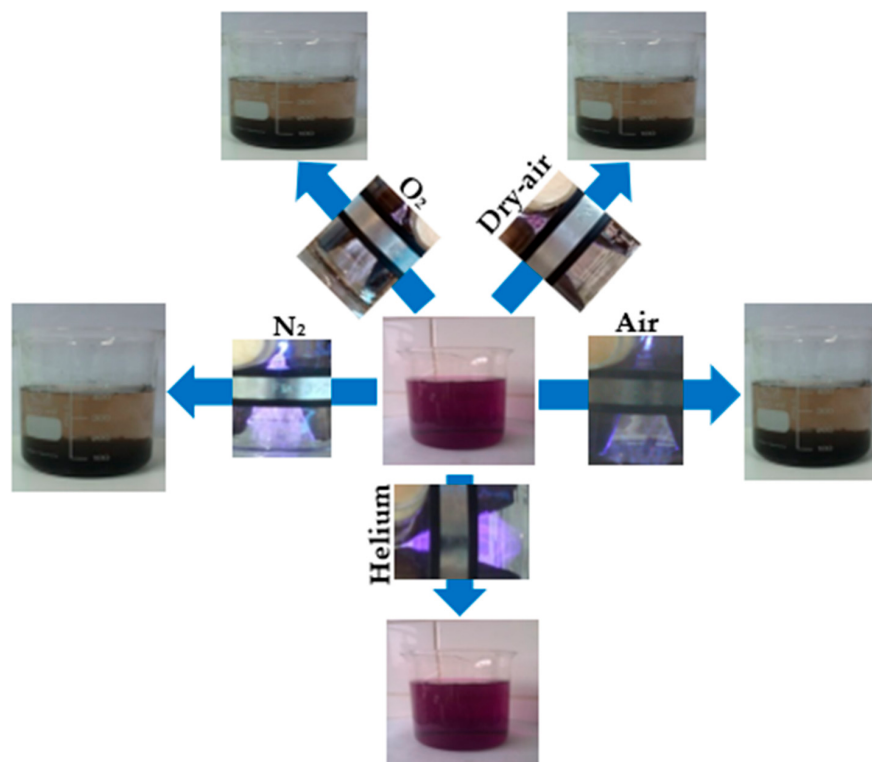


Figure 1. KMnO_4 solution before/after plasma glidarc treatment with different gases.

The influence of plasmagenic gas on the plasma reduction time has been investigated. The precipitation time of KMnO_4 is 15, 22, 22 and 44 min, respectively, with moist air, dry air, N_2 and O_2 (Figure 2), whose difference in the synthesis time could be ascribed to the quality (reducing force of generated species) and quantity. The strength of the reducing species produced via O_2 as plasmagenic gas is weaker than those of the reducing species generated with the other plasmagenic gases. Furthermore, the depletion of humidification only slightly increases the precipitation time with moist air, O_2 or N_2 , which could be explained by the only weak impact of gas humidification on the production of reducing species, consistent with the only weak color change in the plasma plume after humidification depletion (Figure S1). MnO_4^- may react with H_2O_2 from ($\text{HO}_2\cdot/\text{H}_2\text{O}_2$, $E^\circ = 1.44\text{ V}$) or with H_2O_2 from ($\text{O}_2/\text{H}_2\text{O}_2$, $E^\circ = 0.69\text{ V}$) when O_2 is used as plasmagenic gas (Table 1). However, MnO_4^- ($E^\circ(\text{KMnO}_4/\text{MnO}_2) = 1.70\text{ V}$) reacts with H_2O_2 from ($\text{O}_2/\text{H}_2\text{O}_2$, $E^\circ = 0.69\text{ V}$) couple, which is the major reaction, i.e., the one with the largest value of thermodynamic constant (or biggest value of the difference between potential redox of two considered equations). Furthermore, $\text{HO}_2\cdot$ would be one of the products of the reaction between MnO_4^- and H_2O_2 from ($\text{HO}_2\cdot/\text{H}_2\text{O}_2$, $E^\circ = 1.44\text{ V}$), which is inconsistent with the short lifetime of this radical. The longer synthesis time of MnO_2 with O_2 gas may be explained by the weak production of H_2O_2 ($\text{O}_2/\text{H}_2\text{O}_2$, $E^\circ = 0.69\text{ V}$) species compared to the other plasmagenic gases containing nitrogen, which generate massive concentrations of HNO_2 (NO_2/HNO_2 , $E^\circ = 0.51\text{ V}$) and greater reducing potential than H_2O_2 . Even if O_2 as plasmagenic gas inducing 44 min for complete precipitation seems higher, gliding arc plasma still appears as an effective method faced with classical ones, which require long synthesis times, sometimes 5 h or more, and,

in some cases, the use of the organic surfactants [3,4,6]. Table 2 shows the values of the final pH of the solution after the precipitation of KMnO₄ solution with different gases. We recorded a significant decrease in the initial solution pH (7.7) to about 2.5. Compared to moist air, dry air or N₂, which produces the NO· radical known as acidifying species (HNO₂ + HNO₃), we expected a smaller pH solution drop with O₂ gas [19–21]. Nonetheless, the long synthesis time with O₂ might have produced more acidifying species (H⁺) [22] and could explain the final pH value of 2.58 that was comparable to those with other gases. Moreover, humidification (bubbling) does not significantly affect the pH solution (Table 2).

Table 1. Species responsible of KMnO₄ reduction with different gases [10,12,19–22].

Moist Air (Atmospheric Air)	
With bubbling	Without bubbling
$N_2 + e^- \rightarrow 2N\cdot + e^-$ $O_2 + e^- \rightarrow 2O\cdot + e^-$ $N\cdot + O\cdot \rightarrow NO\cdot$ $N_2 + O\cdot \rightarrow NO\cdot + N\cdot$ $H_2O_{(g+l)} + e^- \rightarrow H\cdot + HO\cdot + e^-$ (bubbling water) $N\cdot + HO\cdot \rightarrow NO\cdot + H\cdot$ $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ($E^\circ = 1.7$ V) $NO\cdot + 2H_2O_{(l)} \rightarrow NO_3^- + 4H^+ + 3e^-$ ($E^\circ = 0.94$ V) $HNO_2 \rightarrow NO_2 + H^+ + e^-$ (0.51 V) $MnO_4^- + NO\cdot \rightarrow MnO_2 + NO_3^-$	$N_2 + e^- \rightarrow 2N\cdot + e^-$ $O_2 + e^- \rightarrow 2O\cdot + e^-$ $N\cdot + O\cdot \rightarrow NO\cdot$ $N_2 + O\cdot \rightarrow NO\cdot + N\cdot$ $H_2O_{(g)} + e^- \rightarrow H\cdot + HO\cdot + e^-$ (Air) $N\cdot + HO\cdot \rightarrow NO\cdot + H\cdot$ $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ($E^\circ = 1.7$ V) $NO\cdot + 2H_2O_{(l)} \rightarrow NO_3^- + 4H^+ + 3e^-$ ($E^\circ = 0.94$ V) $HNO_2 \rightarrow NO_2 + H^+ + e^-$ (0.51 V) $MnO_4^- + NO\cdot \rightarrow MnO_2 + NO_3^-$
Nitrogen (N ₂)	
With bubbling	Without bubbling
$N_2 + e^- \rightarrow 2N_2^+ + 2e^-$ $N_2 + e^- \rightarrow 2N\cdot + e^-$ $H_2O_{(g+l)} + e^- \rightarrow H\cdot + HO\cdot + e^-$ (bubbling water) $N\cdot + HO\cdot \rightarrow NO\cdot + H\cdot$ $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ($E^\circ = 1.7$ V) $NO\cdot + 2H_2O_{(l)} \rightarrow NO_3^- + 4H^+ + 3e^-$ ($E^\circ = 0.94$ V) $HNO_2 \rightarrow NO_2 + H^+ + e^-$ (0.51 V) $MnO_4^- + NO\cdot \rightarrow MnO_2 + NO_3^-$	$N_2 + e^- \rightarrow 2N_2^+ + 2e^-$ $N_2 + e^- \rightarrow 2N\cdot + e^-$ $H_2O_{(l)} + e^- \rightarrow H\cdot + HO\cdot + e^-$ (reaction medium) $N\cdot + HO\cdot \rightarrow NO\cdot + H\cdot$ $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ($E^\circ = 1.7$ V) $NO\cdot + 2H_2O_{(l)} \rightarrow NO_3^- + 4H^+ + 3e^-$ ($E^\circ = 0.94$ V) $HNO_2 \rightarrow NO_2 + H^+ + e^-$ (0.51 V) $MnO_4^- + NO\cdot \rightarrow MnO_2 + NO_3^-$
Oxygen (O ₂)	
With bubbling	Without bubbling
$O_2 + e^- \rightarrow 2O\cdot + e^-$ $H_2O_{(l)} + e^- \rightarrow H\cdot + HO\cdot + e^-$ (bubbling and air) $H_2O_{(l)} + e^- \rightarrow H^+ + HO\cdot + 2e^-$ $O_2 + O\cdot \rightarrow O_3$ (unfavourable in the presence of water) $O_2 + H\cdot \rightarrow HO_2\cdot$ $HO\cdot + HO\cdot \rightarrow H_2O_2$ (reducing species) $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ ($E^\circ = 2.07$ V) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ($E^\circ = 1.7$ V) $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ ($E^\circ = 0.69$ V) $2MnO_4^- + 3H_2O_2 + 2H^+ \rightarrow 2MnO_2 + 3O_2 + 4H_2O$	$O_2 + e^- \rightarrow 2O\cdot + e^-$ $H_2O_{(l)} + e^- \rightarrow H\cdot + HO\cdot + e^-$ (from air) $H_2O_{(l)} + e^- \rightarrow H^+ + HO\cdot + 2e^-$ $O_2 + O\cdot \rightarrow O_3$ $O_2 + H\cdot \rightarrow HO_2\cdot$ $HO\cdot + HO\cdot \rightarrow H_2O_2$ $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ ($E^\circ = 2.07$ V) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ($E^\circ = 1.7$ V) $H_2O_2 \rightarrow HO_2 + H^+ + e^-$ ($E^\circ = 1.44$ V) $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ ($E^\circ = 0.69$ V) $2MnO_4^- + 3H_2O_2 + 2H^+ \rightarrow 2MnO_2 + 3O_2 + 4H_2O$
Dry-air (N ₂ + O ₂)	
$N_2 + e^- \rightarrow 2N\cdot + e^-$ $O_2 + e^- \rightarrow 2O\cdot + e^-$ $N\cdot + O\cdot \rightarrow NO\cdot$ $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ($E^\circ = 1.7$ V) $NO\cdot + 2H_2O_{(l)} \rightarrow NO_3^- + 4H^+ + 3e^-$ ($E^\circ = 0.94$ V) $HNO_2 \rightarrow NO_2 + H^+ + e^-$ (0.51 V) $MnO_4^- + NO\cdot \rightarrow MnO_2 + NO_3^-$	

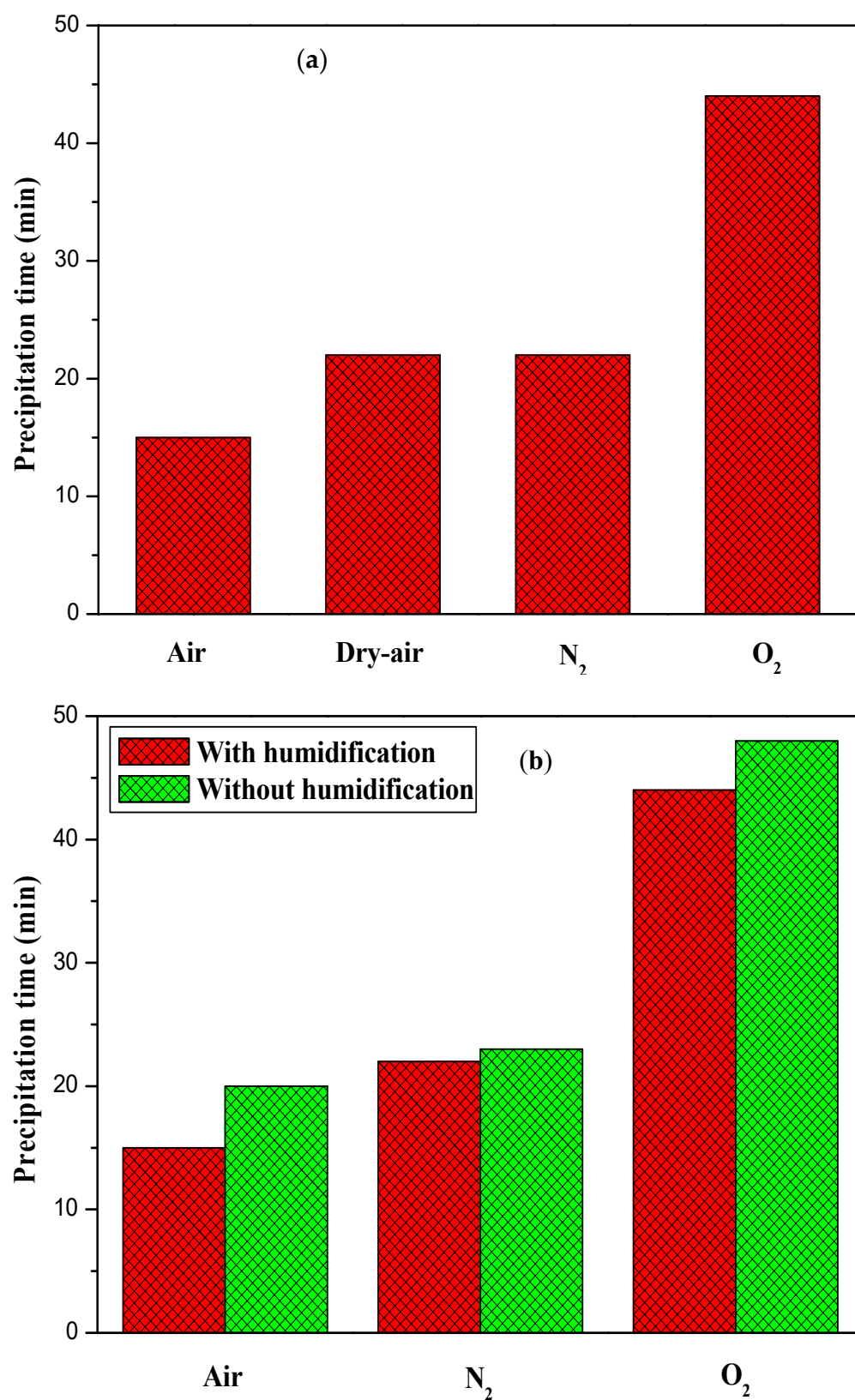


Figure 2. Influence of plasmagenic gas (a) and humidification (b) on precipitation time.

Table 2. Final pH of the solution with different plasmagenic gases (initial pH = 7.7).

Gas	Final pH of the Solution	
	With Humidification	Without Humidification
Dry-air	-----	2.63
Air	2.50	2.52
N ₂	2.81	2.70
O ₂	2.58	2.58

2.2. Characterizations of Prepared Materials

The XRD patterns of the as-synthesized materials with and without gas humidification are shown in Figure 3a. All XRD patterns are comparable, with all peaks indexed to either α -MnO₂ (JCPDS 44-0141), called Cryptomelane [27–29], and/or to γ -MnO₂ (JCPDS 14-0644), called Nsutite [29–31]. These peaks may indicate a mixture of the two polymorphs with a bit more γ . Therefore, even though the reported synthesis duration varies, a change in plasmagenic gas has no effect on the crystalline structure of plasma-synthesized MnO₂ (Figure 3a). Different synthesis times and polymorphs are caused by variations in airflow or voltage during the plasma synthesis of MnO₂, according to Boyom et al. [8]. Could we, therefore, attribute this unchanged crystalline structure to the high initial precursor concentration that causes the first generated α -MnO₂ to be converted to the γ -MnO₂ polymorph? To challenge this hypothesis, we reduced the precursor concentration from 700 to 350 mg/L. Despite the difference in precipitation time, the XRD patterns of the materials obtained after precipitation of KMnO₄ starting concentration values of 350 and 700 mg/L with the humidified air as plasmagenic gas are almost identical (Figure 3b). The difference in peak intensities at 12 and 22° could illustrate the different rates of α -MnO₂ and γ -MnO₂ polymorph component materials represented by both XRD patterns. Another possible explanation could be that the high-power energy range of (288–336W) may induce a greater production of short-lived (NO·) and long-lived (NO₂[−]) reactive species during the current investigation, as opposed to earlier studies (100 W) [8,9]. Therefore, the first produced precipitate (α -MnO₂) is converted into (γ -MnO₂) through the maturation process of the crystallites [32].

FTIR spectra of all plasma-synthesized MnO₂ have been recorded (Figure 4). The stretching and bending vibrations of the H-O bonds of the physisorption water are responsible for the absorption bands located around 3370, 1640, and 1045 cm^{−1}. The vibration of the chemisorbed water's H-O bond is responsible for the band at 1390 cm^{−1}. It is challenging to attribute this absorption band to NO₃[−], as Chalmers did [33]. We are aware that NO₃[−] species are generated in solution during plasma glidarc discharge with nitrogenous gas. Nonetheless, given that O₂ gas cannot produce nitrogen species [22] and that the band at 1390 cm^{−1} is also present in the spectrum of MnO₂ that has been plasma synthesized with O₂, it is perhaps more relevant to attribute this band to the H-O bond of chemisorbed water.

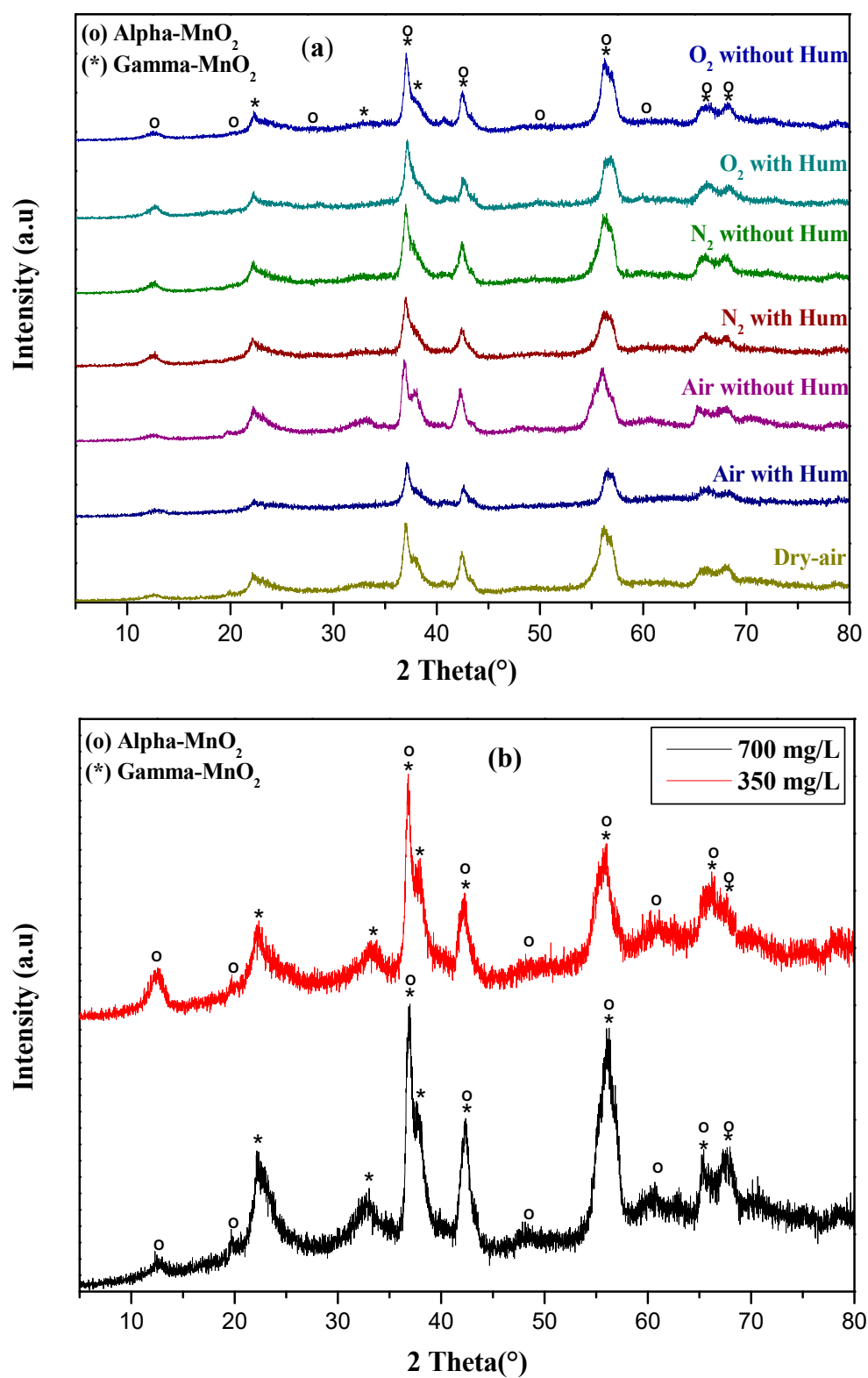


Figure 3. XRD patterns of plasma-synthesized MnO_2 : (a) through different plasmagenic gas with and without humidification, (b) through different initial concentration of KMnO_4 with moist air as plasmagenic gas.

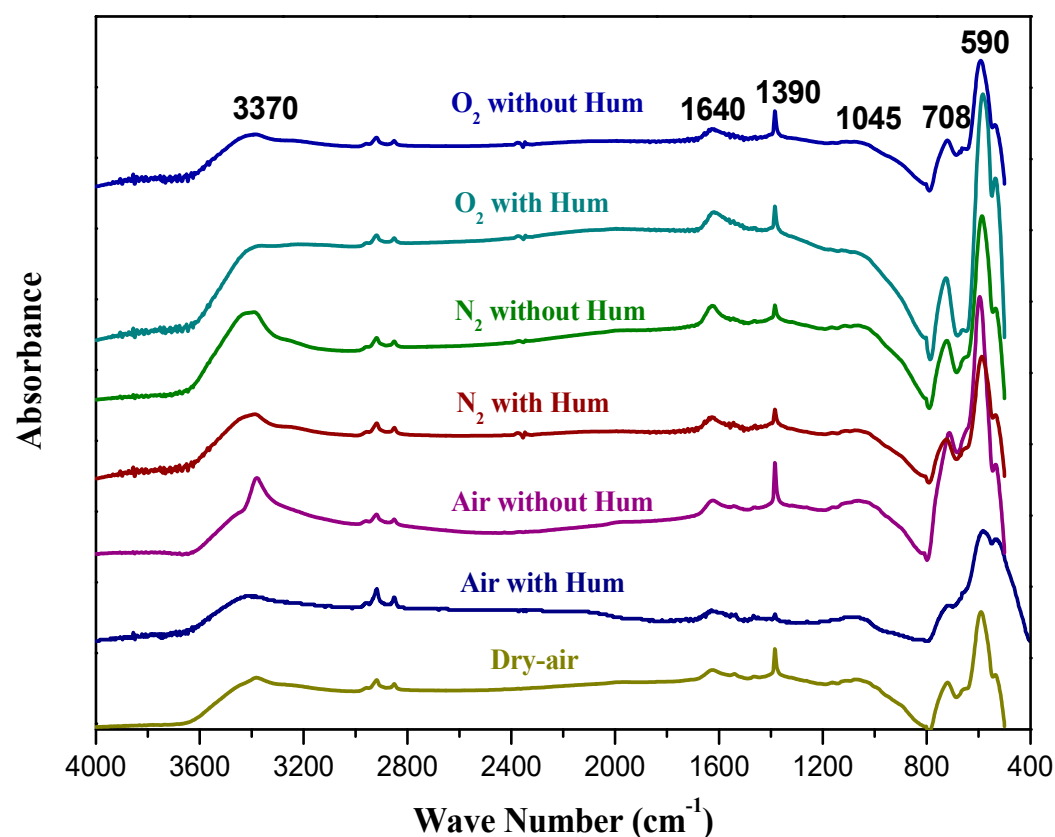


Figure 4. FTIR spectra of plasma-synthesized MnO₂ with different plasmagenic gases.

The surface properties of plasma-synthesized MnO₂ with different gases were investigated using XPS (Figures S2–S4) and nitrogen physisorption (adsorption–desorption isotherms in Figure 5) analyses. Figure S2 shows the survey spectra of different prepared MnO₂, displaying Mn2s, Mn3s, K2p, C1s, Mn2p and Mn3p elements. Table 3 summarizes the XPS findings. The spin separation values ($\Delta\text{Mn}2p$) between Mn2p_{1/2} and Mn2p_{3/2} peaks (Figure S3) within each prepared material are in accordance with the literature data on MnO₂ and illustrate the important presence of Mn(+IV) [8]. The AOS of Mn values reveals Mn in mixed valence (+III, +IV) [34]. Therefore, the charge compensation of Mn(+III) is assured by K⁺ species inserted within the largest tunnels ($0.46\text{\AA} \times 0.46\text{\AA}$) of $\alpha\text{-MnO}_2$ [1,8]. In addition, plasma-synthesized MnO₂ with pure O₂ gas also revealed the presence of nitrogen elements in trace, contrary to what has been previously mentioned [22]. According to Burlica et al., when O₂ is used as plasmagenic gas, no nitrogen species are produced [22]. This trace of the nitrogen element with O₂ gas as operating conditions may be due to atmospheric air, which would get, inadvertently, into the reactor. O1s spectra of prepared MnO₂ through different plasmagenic gases reveal three types of oxygen (Figure S4), with structural or lattice oxygen O_β (in the form of O^{2−}) appearing in the binding energy range of 529.7–530.1 eV. The second is chemisorbed oxygen O_α (in the form of O₂^{2−}, HO[−]) at the surface falling within the 531.3–531.8 eV range, which is chemically bonded at the surface of each material with more actives than O_β, thanks to their higher mobility. The third is oxygen from carbon contamination O_γ present within the 532.4–533.2 eV range [8]. Plasma-synthesized MnO₂ via nitrogen gas without humidification exhibits a lower density of oxygen vacant sites (O_α/O_β). This could be explained by the depletion of humidification and absence of oxygen within plasmagenic gas, which could result in a lower presence of chemisorbed oxygen (O_α) at the material's surface than lattice oxygen (O_β). Thus, plasma-generated N[•] and N₂⁺ species probably consume oxygen in solution and could explain the decreased value of O_α/O_β. The remaining materials are obtained from plasmagenic gas

components that partially or totally contain molecular oxygen. This may limit the amount of oxygen consumed in solution and likely explains why the O_{α}/O_{β} values are higher than those of MnO_2 obtained from N_2 without humidification. Furthermore, Table 4 displays the specific surface areas of all plasma-synthesized MnO_2 using various plasmagenic gases. The material produced using humidified air had a greater specific surface area. As previously mentioned, the plasma synthesis time increases following the gas order moist air (15 min), dry air (22 min), N_2 (22 min) and O_2 (44 min), respectively, with specific surface areas of 116, 55, 64 and 93 m^2/g . As a result, the specific surface area decreases from moist air to dry air and then increases from dry air to O_2 . The specific surface area decreases as gas humidification is removed. We would have expected to see an increase in the specific surface area with longer synthesis times, meaning that the latter should develop more active sites. Boyom et al. demonstrated that lowering the voltage or airflow during the plasma reduction of Mn^{7+} or -oxidation of Mn^{3+} causes an increase in the synthesis time and results in a notable increase in the specific surface area [8]. As a result, extending the MnO_2 's plasma synthesis period does not always result in an increase in its specific surface area; this could be because of a change in the crystalline structure. In our investigation, the change in the plasmagenic gas and depletion of humidification do not induce any change in the crystalline structure. Figure 6 shows adsorption–desorption isotherms of type IV for all plasma-synthesized MnO_2 whatever the plasmagenic gas and with humidification or not. Both materials that were obtained using atmospheric air or humidified oxygen exhibit hysteresis loops between 0.6 and 1.0 relative pressure, potentially illustrating the presence of mesopores. The rest of the materials show hysteresis loops at greater relative pressure, attesting the presence of larger mesopores between larger particles, which is consistent with their lower specific surface area values compared to the two previous ones. In summary, atmospheric air seems to be the most effective plasmagenic gas for plasma-synthesized MnO_2 because it is cost-free, permits a brief plasma reduction time of $KMnO_4$ and exhibits a greater specific surface area.

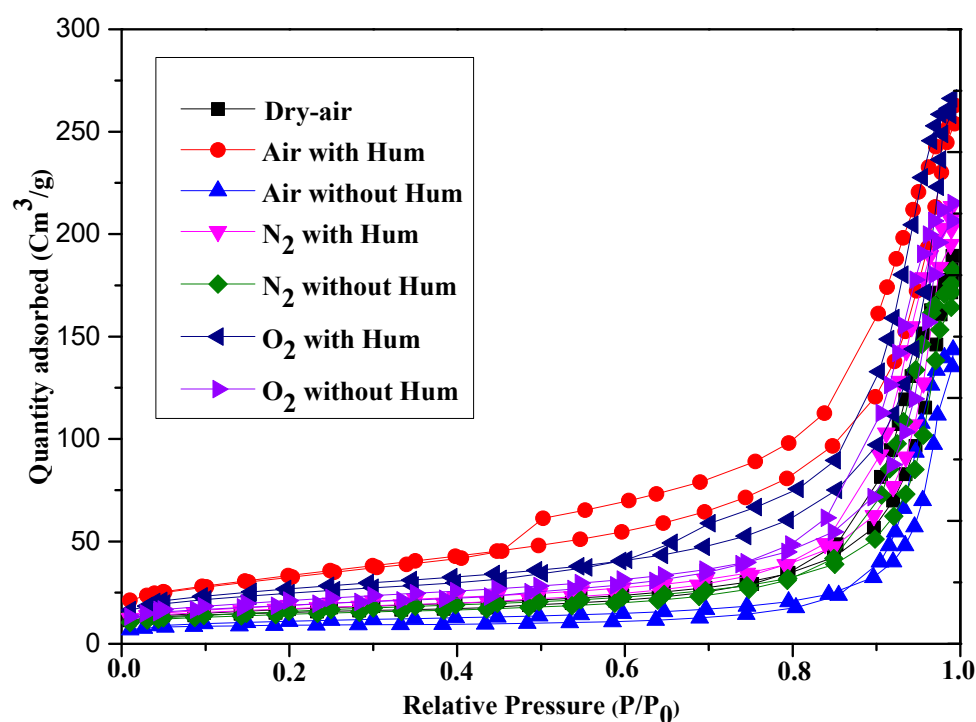


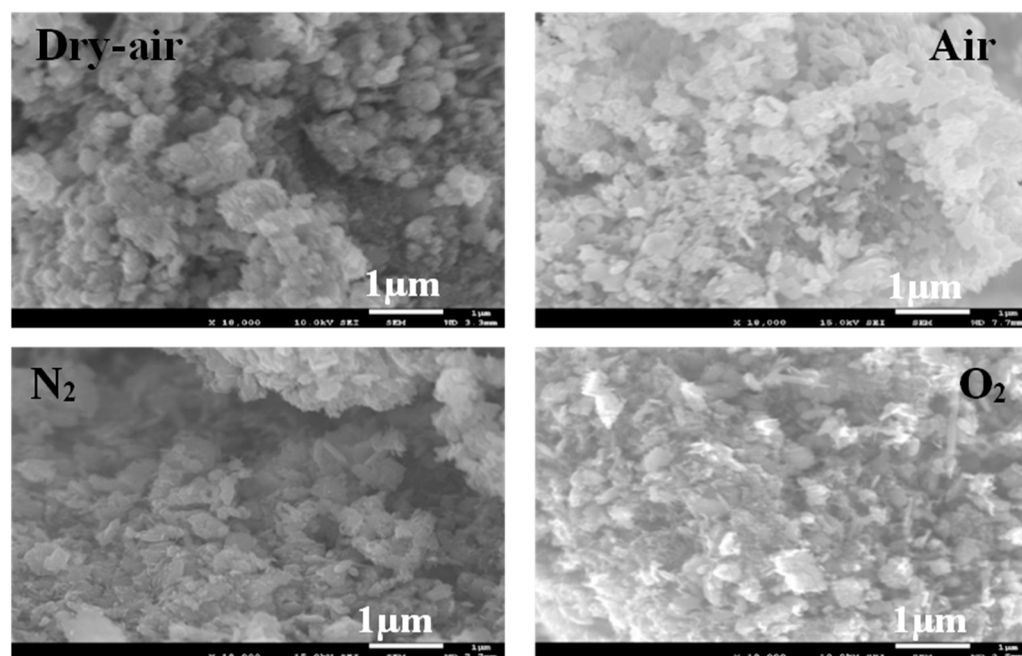
Figure 5. Adsorption–desorption isotherms of plasma-synthesized MnO_2 with different gases.

Table 3. XPS data of different plasma-synthesized MnO₂.

Material (MnO ₂)	AOS (Mn)	%N	O _α /O _β	Mn2p _{1/2} (eV)	Mn2p _{3/2} (eV)	ΔMn2p (eV)
Dry-air	3.41	1.2	0.55	653.86	642.27	11.59
Air with Hum	3.43	1.3	0.54	653.82	642.20	11.62
Air without Hum	3.39	1.6	0.60	653.80	642.27	11.53
N ₂ with Hum	3.38	1.1	0.61	653.86	642.24	11.62
N ₂ without Hum	3.40	1.2	0.35	653.82	642.41	11.41
O ₂ with Hum	3.35	Trace	0.64	653.89	642.24	11.65
O ₂ without Hum	3.41	Trace	0.57	653.89	642.39	11.50

Table 4. Nitrogen physisorption data of different plasma-synthesized MnO₂.

Material (MnO ₂)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)
Dry-air	56	0.28	21
Air with Hum	116	0.38	11
Air without Hum	37	0.22	29
N ₂ with Hum	64	0.32	21
N ₂ without Hum	54	0.27	22
O ₂ with Hum	93	0.41	16
O ₂ without Hum	73	0.33	18

**Figure 6.** SEM images (×18,000) of plasma-synthesized MnO₂ using different gases.

SEM images are shown in Figure 6. Plasma-synthesized MnO_2 via moist air, N_2 , dry air or O_2 gas shows agglomerated particles (aggregates particles) with irregular morphology. As a result, changing the plasmagenic gas has no effect on the product's shape, supporting the consistency of all XRD patterns obtained and maybe explaining why the nucleation process remains the same [32]. This corroborates the adsorption–desorption isotherm shapes (Figure 5), and it may also help to explain why the specific surface area of MnO_2 acquired by atmospheric air was higher than that of the other materials (Table 4). This suggests that nanoflakes would develop greater specific surface area than rods. Given the different plasma reduction times of KMnO_4 solution and the corresponding textural data (specific surface area, porosity) of the obtained products, we can conclude that compressed atmospheric air is the best plasma gas, due to its availability and free cost, which is advantageous from an economical standpoint.

2.3. Catalytic Treatment of Benzene

The benzene catalytic conversion progression with temperature for the four plasma-synthesized MnO_2 without plasmagenic gas humidification is displayed in Figure 7a. With plasma-synthesized MnO_2/O_2 ($73 \text{ m}^2/\text{g}$), MnO_2/air ($37 \text{ m}^2/\text{g}$), $\text{MnO}_2/\text{dry air}$ ($56 \text{ m}^2/\text{g}$) and MnO_2/N_2 ($54 \text{ m}^2/\text{g}$), conversion degrees of 87, 92, 98 and 100% were, respectively, attained at 250°C . Despite having smaller specific surface areas than MnO_2 produced from O_2 gas, there is an almost complete conversion of benzene with plasma-synthesized MnO_2 using dry air and N_2 . We expected a difference in benzene conversion given the notable discrepancy between the respective specific surface area values (MnO_2 obtained without gas humidification), particularly for plasma-synthesized MnO_2 with O_2 , which showed the greatest specific surface area value (Table 4). This fact can, therefore, be explained by the diameter of the pore, shown in Table 4, where the MnO_2 obtained by dry air or N_2 has a larger pore diameter (21 nm) than the MnO_2 obtained by air (11 nm) or O_2 (16 nm). However, the material's crystalline structure should be considered in addition to its surface area. As we know, $\alpha\text{-MnO}_2$ ($4.6\text{\AA} \times 4.6\text{\AA}$ tunnels) together with $\gamma\text{-MnO}_2$ ($2.3\text{\AA} \times 4.6\text{\AA}$ and $2.3\text{\AA} \times 4.6\text{\AA}$ tunnels) make up all plasma-synthesized MnO_2 (Figure 3a). The catalytic oxidation of benzene would be possible within the channel of the largest $\alpha\text{-MnO}_2$ tunnels. According to Boyom et al., the catalytic bleaching degrees of Tartrazin Yellow dye in solution with $\alpha\text{-MnO}_2$ ($98 \text{ m}^2/\text{g}$) and mixed $\alpha\text{-MnO}_2 + \gamma\text{-MnO}_2$ ($141 \text{ m}^2/\text{g}$) as catalysts were nearly equal [29]. Therefore, despite the highest specific surface area of MnO_2 ($\alpha + \gamma$) obtained via air, it is likely to have a much lower amount of $\alpha\text{-MnO}_2$ than $\gamma\text{-MnO}_2$, which would lower the catalytic efficiency. However, as compared to the blank test (no catalyst), each of the four plasma-synthesized MnO_2 showed a higher benzene conversion, highlighting their positive activities. According to plasma-synthesized MnO_2/O_2 , MnO_2/air , $\text{MnO}_2/\text{dry air}$, and MnO_2/N_2 , the temperature of 50% benzene conversion T_{50} is 220, 220, 215, and 210°C , respectively. These values are nearly identical. Using a $\text{MnO}_x\text{-CeO}_2$ ($124 \text{ m}^2/\text{g}$) mixed oxide catalyst made through co-precipitation, Tang et al. achieved a T_{50} at 265°C and a full conversion of benzene (200 ppm) to CO_2 and H_2O at 375°C [35]. While our two plasma-synthesized MnO_2 using dry air and N_2 had specific surfaces areas of 56 and $64 \text{ m}^2/\text{g}$, respectively, they reached T_{50} of 215 and 210°C and a complete conversion of benzene (150 ppm) at 250°C , temperatures that are significantly lower than those used by Tang et al. [35]. Using the impregnation approach, Bertinchamps et al. prepared three MnO_x -based catalysts supported on TiO_2 , Al_2O_3 and SiO_2 for the catalytic oxidation of benzene (100 ppm). At 250°C , they achieved conversions of 35, 24 and 55%, respectively,

and at 300–350 °C, they achieved full conversion [5]. MoO_3 (53 m²/g) and $\text{WO}_3\text{-V}_2\text{O}_5/\text{TiO}_2$ (93 m²/g) catalysts were prepared by Debecker et al. using the nonhydrolytic sol–gel route for the catalytic oxidation of benzene (100 ppm) at 300 °C. They achieved conversions of 95 and 97%, respectively [36], but at higher temperatures than that at which our four plasma-synthesized MnO_2 reached complete conversion. For the catalytic oxidation of benzene (100 ppm), Delaigle et al. also generated $\text{Ag-VO}_x/\text{TiO}_2$ (38.2 m²/g) via the impregnation method, reaching a higher conversion degree of 53% at 250 °C [13], which is extremely low in comparison to those obtained using our four plasma-synthesized catalysts. Based on this, we may conclude that gliding arc plasma is a viable catalyst synthesis route for improving the catalytic oxidation of benzene. Otherwise, the effect of the plasma-synthesized MnO_2 's crystalline structure on the catalytic conversion of benzene has been investigated, in contrast to the work mentioned above, in which all four of our synthesized catalysts share the same polymorphic structure. Consequently, we employed three polymorphs of plasma-synthesized MnO_2 according to the protocol described by Boyom et al., $\alpha\text{-MnO}_2$ (98 m²/g) [8] and $\gamma\text{-MnO}_2$ (48 m²/g) [8], both with tunnel structures, and $\delta\text{-MnO}_2$ (186 m²/g) [8], which has a sheet structure. Despite having a lower specific surface area than $\delta\text{-MnO}_2$, Figure 7b shows that during the catalytic oxidation of benzene, $\alpha\text{-MnO}_2$ and $\delta\text{-MnO}_2$ showed nearly identical trends. Consequently, the tunnel structure is more common than the sheet's structure. Looking at $\alpha\text{-MnO}_2$ and $\gamma\text{-MnO}_2$ with their similar structures (tunnels), however, we can see that $\alpha\text{-MnO}_2$ shows a greater catalytic oxidation of benzene than $\gamma\text{-MnO}_2$. This could be because $\alpha\text{-MnO}_2$ has larger tunnels and a higher specific surface area. When Tartrazin Yellow was catalytically oxidized in the liquid phase, these three MnO_2 polymorphs displayed an identical trend [8].

The crystalline structure evolution of MnO_2 produced by plasma following the catalytic oxidation of benzene is shown in Figure 8. Following the catalytic oxidation of benzene, all mixtures of polymorphs ($\alpha + \beta$)- MnO_2 are transformed into $\beta\text{-MnO}_2$ (Figure 8a). The $\alpha\text{-MnO}_2$ polymorph should be present following the catalytic oxidation of benzene. The first explanation for this could be because the four plasma-synthesized MnO_2 with various gases had weaker $\alpha\text{-MnO}_2$ than $\gamma\text{-MnO}_2$. Secondly, K^+ species from the precursor (KMnO_4) could not be present in the channel of the huge amount of $\gamma\text{-MnO}_2$ with tunnel diameters of $2.3\text{\AA} \times 2.3\text{\AA}$ and $2.3\text{\AA} \times 4.6\text{\AA}$ [29], which might stabilize its structure during the catalytic oxidation of benzene. For an effective catalytic process in the gas or liquid phase, this further emphasizes the need for cationic insertion into MnO_2 channels during its synthesis. In contrast to $\gamma\text{-MnO}_2$, which is transformed into $\beta\text{-MnO}_2$ following the catalytic oxidation of benzene to 400 °C, Figure 8b shows the excellent stability of single $\alpha\text{-MnO}_2$ or $\delta\text{-MnO}_2$. Consequently, during the catalytic oxidation of benzene, K^+ present in ($4.6\text{\AA} \times 4.6\text{\AA}$) tunnels of $\alpha\text{-MnO}_2$ and between the sheets of $\delta\text{-MnO}_2$ stabilizes both materials. In contrast to $\gamma\text{-MnO}_2$ (which has no cationic species in its channels), which is transformed into $\beta\text{-MnO}_2$ after calcination at 400 °C and loses its catalytic activity after the first cycle, Boyom et al. (2023) reported a high crystalline stability of $\alpha\text{-MnO}_2$ (K^+ within its channels) during calcination until 400 °C and catalytic stability in the liquid phase over four cycles [1].

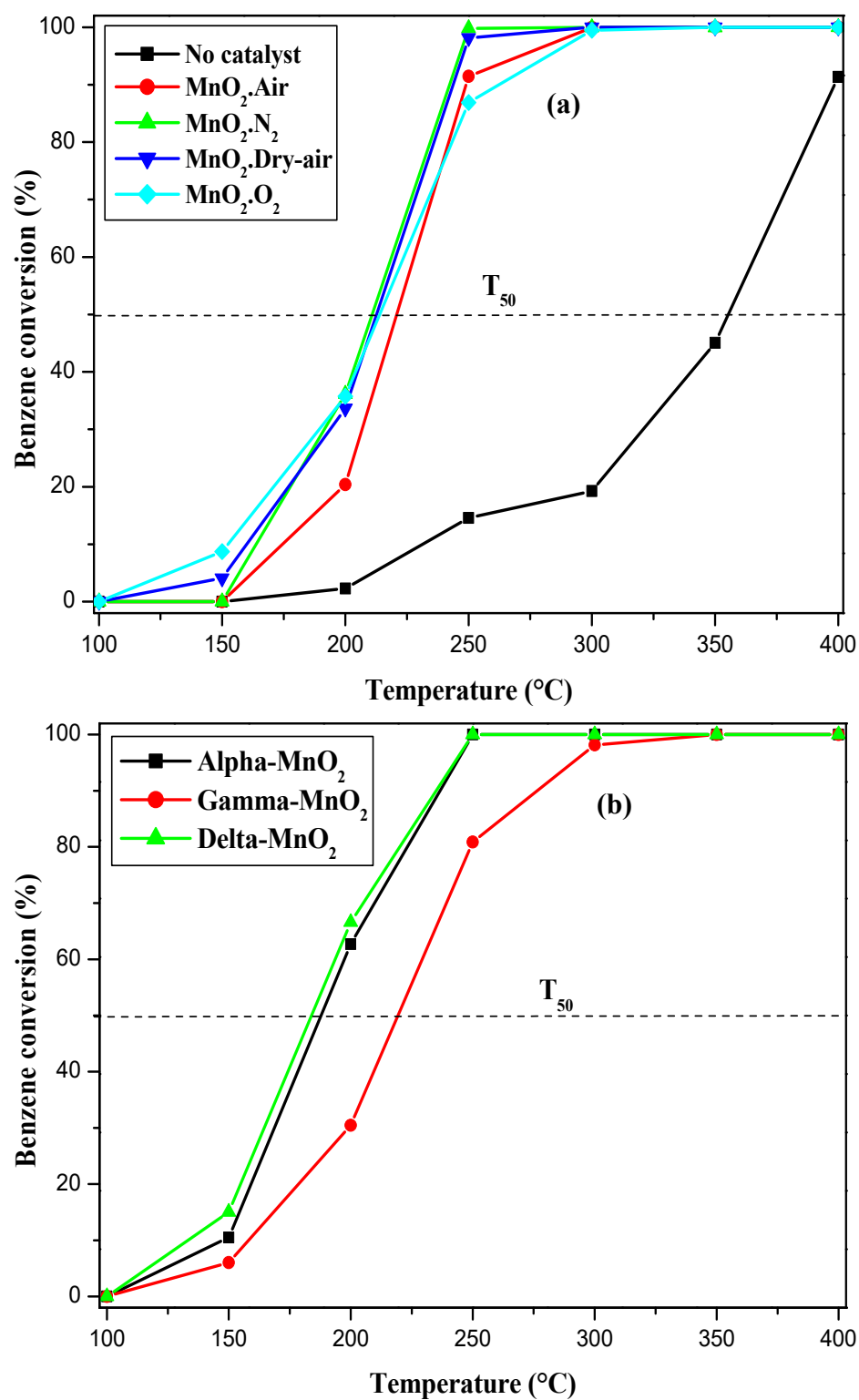


Figure 7. (a) Benzene conversion with plasma-synthesized MnO_2 for different plasmagenic gases without humification, (b) impact of MnO_2 crystalline structure.

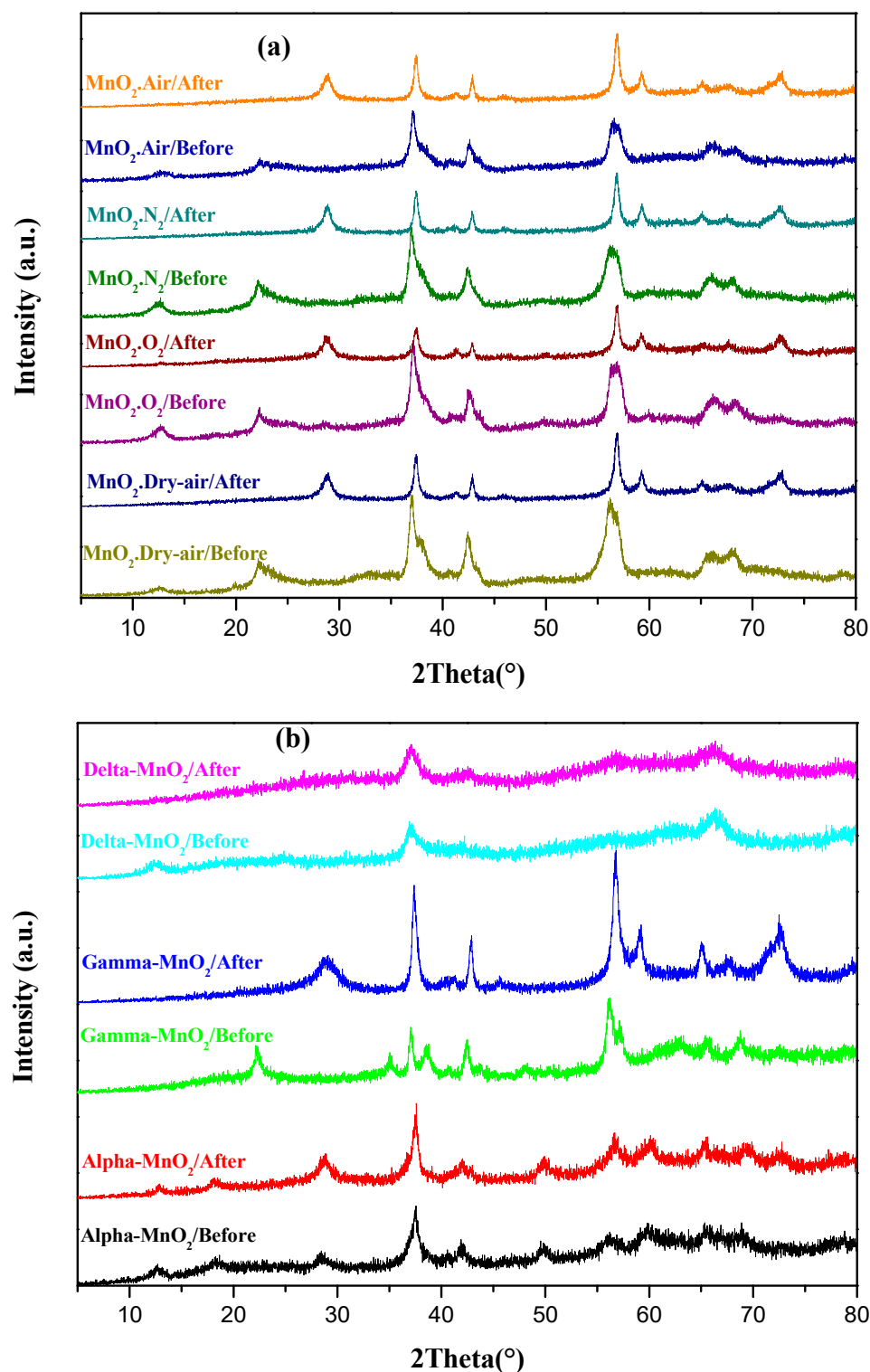


Figure 8. XRD patterns of plasma-synthesized MnO_2 before and after oxidation of benzene: (a) The same polymorphs (b) Different polymorphs.

3. Experimental Strategy

3.1. Gliding Arc Plasma as Synthesis Device

Figure 9 represents the experimental synthesis device. Briefly, the feeding “plasma-genic” gas (air, dry air, He, N_2 or O_2) is supplied (450 L/h) via an air compressor. Before being injected along the aluminum electrodes through a nozzle, the gas goes through a bubbler that contains deionized water and is humidified. However, the dry-air gas was

used without humidification. The electrodes are connected to a high-voltage transformer (AC 240 V/4.5 kV—4.31 A), which delivers a mean current intensity range of 130 mA (2400 V), in operating conditions. Then, an electric arc is created at the smallest electrode gap, when the high voltage is applied. This arc is pushed away by the flow of gas (450 L/h) from the nozzle and glides along the electrodes, until it collapses. A new arc is created, and the cycle restarts again as a large plasma plume in contact with the liquid surface.

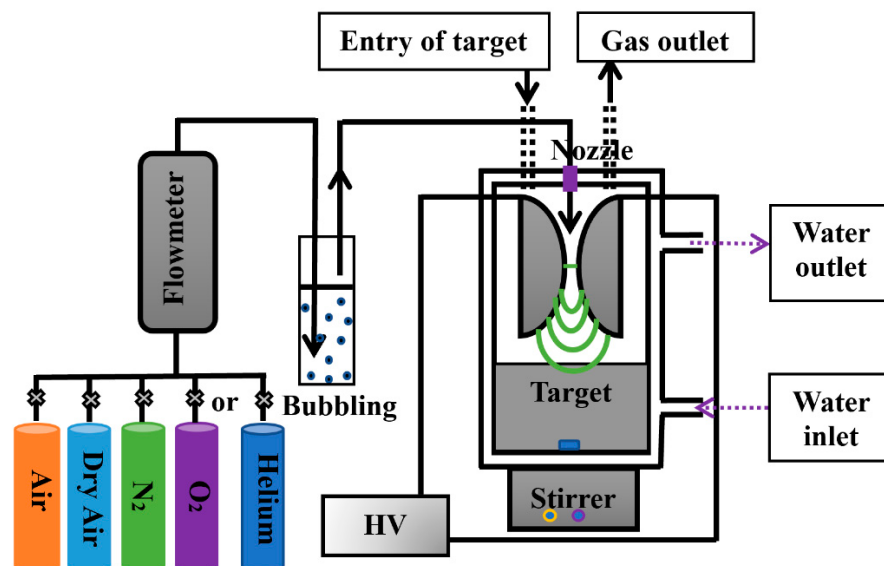


Figure 9. Experimental scheme of gliding arc plasma setup.

3.2. Synthesis Procedures

Precursors used include KMnO_4 (99% Roth company, Keerbergen, Belgium), while the plasmagenic (feeding) gases used are moist air, dry air (80% N_2 + 20% O_2), N_2 (99.999%), O_2 (99.999%) and helium (99.999%). The target solutions of each precursor (450 mL, 700 mg/L) were exposed to plasma discharge under magnetic stirring, until complete precipitation. Simple filtration was used to recover the brown-black precipitate, and it was washed with deionized water several times before drying in an oven under air at 105 °C.

3.3. Characterization Techniques

X-ray diffraction patterns of the different materials were recorded between 5 and 80° at a rate of 0.6°/min with an increment of 0.02° and an integration time of 2 s using a D8 ADVANCE BRUKER diffractometer, operating at 40 kV and 40 mA, with $\text{Cu K}\alpha$ radiation (1.5418 Å). Crystalline phases were identified using the ICDD-JCPDS database.

Fourier-transform infrared spectroscopy was recorded in transmission mode after 100 scans, at a resolution of 4 cm^{-1} , with an Equinox IFS55 spectrometer (Bruker, Billerica, MA, USA) equipped with a DTGS detector. To make the pellets, the samples were diluted (1 wt% in KBr) and then pressed into self-supporting disks using a hydraulic press (5–7.5 tons) for approximately 5 min. As a reference, the atmospheric air spectrum was utilized.

X-ray photoelectron spectroscopy was carried out using an Axis Ultra (SSX-100/206) spectrometer (Surface Science Instruments, Mountain View, CA, USA) equipped with a 30° solid acceptance lens, a hemispherical analyzer, and a monochromatic source of $\text{Al K}\alpha$ (1486.6 eV) operating at 15 kV and 10 mA. The pressure inside the analysis chamber was approximately 10^{-6} Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The area being analyzed was about 1.4 mm^2 and the pass energy was set to 150 eV. In these conditions, the full width at half maximum (FWHM) of the

Au 4f_{7/2} peak of a clean gold standard sample was about 1.6 eV. Charge stabilization was achieved by using a flood gun at 8 eV and a nickel (Ni) grid placed 3 mm above the sample surface. The sample powder was pressed into small stainless-steel troughs with a diameter of 4 mm and placed in an aluminum-conductive carousel. All samples were outgassed overnight in a vacuum (10^{−5} Pa) prior to analysis. The binding energy scale was calibrated, taking the carbon C1s peak fixed at 284.8 eV (aliphatic component of carbon contamination) as reference. Peak areas were normalized based on acquisition parameters and experimental sensitivity factors provided by the manufacturer to obtain atomic ratios. The Mn2p region was used to quantify Mn proportion. After determining the oxygen related to contamination carbon, the O1s signal was used to calculate the proportion of lattice oxygen (structural) and chemisorbed oxygen (surface). The Mn average oxidation state (AOS) was determined using the shift in the Mn3s binding energy [6], following Equation (1) [6].

$$\text{AOS} = 8.956 - 1.126 \Delta E_s \quad (1)$$

where ΔE_s represents the shift in the binding energy between Mn3s and its satellite.

Nitrogen physisorption was carried out at −196 °C using a Micromeritics Tristar 3000 (Micromeritics, Norcross, GA, USA) over a relative pressure range [10^{−6}–0.99]. Before analysis, 150 mg of sample was outgassed at 150 °C for 12 h under primary vacuum. The specific surface area and pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) equation in the 0.05–0.30 P/P₀ range and the Barrett–Joyner–Halenda (BJH) method, respectively. The morphology was investigated using a LEO 983 GEMINI electron microscope (Thornwood, NY, USA) operated at an acceleration voltage of 10–15 kV depending on the sample. Prior to the analysis, the samples were metallized with a ~15 nm thick layer of chromium under an argon atmosphere.

3.4. Catalytic Tests

Catalytic tests were conducted on benzene (2000 ppm/He) as model pollutant within a metallic fixed-bed reactor (Microactivity Reference, PID Eng&Tech, Madrid, Spain). The reaction was operated at atmospheric pressure. Further, 100 mg of plasma-synthesized MnO₂ (200–315 µm) was used as catalyst, diluted in 400 mg of inactive glass beads (315–500 µm) to prevent hot spot formation. The total gas flow was set at 100 mL/min, comprising 7.5% of benzene (150 ppm), 10% of O₂ (99.999% purity), and 82.5% of helium (99.999% purity). The benzene conversion was tested without adding H₂O or CO₂. The reaction was conducted from 100 to 400 °C in 50 °C increments for 150 min following initial stabilization. The decomposition of benzene was followed using a gas chromatograph (VARIAN CP-3800, Varian, Cary, NC, USA) equipped with an FID detector. The conversion degree of benzene was found, using the concentrations of reactants and products after stabilization (2).

$$\%D = (S_i - S_T) \times 100/S_i \quad (2)$$

where S_i represents the initial peak area of benzene at 100 °C (assuming no conversion at 100 °C) and S_T the peak area of benzene at the different temperatures. No other peaks were observed by FID.

4. Conclusions

We demonstrated in this work that the precipitation reduction of KMnO₄ solution using the gliding arc plasma route is possible, not only with moist air (atmospheric air) but also with other gases, such as dry air, nitrogen (N₂) or oxygen (O₂), but with different exposure times. Therefore, oxygenated species like H₂O₂ produced with O₂ gas can reduce KMnO₄ solution, although NO· radicals produced with moist air, dry air, or N₂ are not

the only reducing species produced in plasma glidarc. Helium gas did not allow for the precipitation of KMnO_4 . Otherwise, the formation of reducing species and, thus, the synthesis time were not considerably impacted by gas humidification. Despite the difference in the synthesis time, the plasmagenic gas did not affect the physicochemical properties of plasma-synthesized MnO_2 . This study demonstrates that using atmospheric air as plasmagenic gas has two benefits: first, it is free, and, second, the short plasma synthesis time and large specific surface area, which are ideal for catalytic oxidation. Therefore, the crystalline structure (polymorph nature/tunnel size) has a considerable impact on the catalytic oxidation of the benzene molecule in addition to the specific surface area. Even if the surface area is unaffected, every plasma-synthesized MnO_2 with the same crystalline structure demonstrated good catalytic oxidation of benzene at low temperatures. Nevertheless, the application of several MnO_2 polymorphs demonstrated the important influence of both the specific surface area and the crystalline structure. In contrast to $\gamma\text{-MnO}_2$, which had a low degree of conversion and was transformed into $\beta\text{-MnO}_2$ polymorph, the $\alpha\text{-MnO}_2$ and $\delta\text{-MnO}_2$ polymorphs both demonstrated the best conversion and higher stability during the catalytic oxidation of benzene. Because of its high degree of benzene conversion and low specific surface area, the $\alpha\text{-MnO}_2$ polymorph with a large tunnel structure would be the ideal catalyst when compared to those of the $\delta\text{-MnO}_2$ polymorph with a sheet structure.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15050451/s1>, Figure S1: Plasma plume colour with and without gas humidification; Figure S2: XPS survey spectra of all plasma-synthesized MnO_2 ; Figure S3: Spin separation of $\text{Mn}2p$ doublet of all plasma-synthesized MnO_2 ; Figure S4: $\text{O}1s$ XPS spectra of plasma-synthesized MnO_2 with different plasmagenic gases.

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