Incorporating Pb$^{2+}$ Templates into the Crystalline Structure of MnO$_2$ Catalyst Supported on Monolith: Applications in H$_2$O$_2$ Decomposition

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ABSTRACT: Several MnO$_2$ catalysts, promoted with Pb$^{2+}$ ions and supported on a wash-coated monolith (WMon), briefly, $x$Pb$_y$Mn-WMon ($x = 0, 0.5, 1.0, 1.5, 2,$ and $2.5$ and $y = 8$ wt %), were prepared. The presence of Pb$^{2+}$ affects the manganese oxidation state, crystalline phase, thermal resistance, metal dispersion, and catalytic performance. According to XPS spectra, XRD patterns and HRTEM images, manganese was dispersed on the monolith surface as Mn$^{3+}$ and Mn$^{4+}$ species in both $\alpha$ and $\beta$ crystalline phases. The ratios of Mn$^{3+}$/Mn$^{4+}$ states and $\alpha$/$\beta$ phases were highly enhanced, and the desired Pb$_x$Mn$_y$O$_{16}$ phase (coronadite) was formed. Concentrations of the defect oxygen (Mn$\sim$O$\sim$H) and oxygen vacancies, which improve the catalyst reducibility and the MnO$_2$ reduction temperature, were also increased. Further, based on the H$_2$ chemisorption analysis, the Pb$^{2+}$ template would increase the manganese dispersion and the reaction sites. Meanwhile, the average MnO$_2$ crystallite size was decreased from 13.26 to 8.15 nm. The optimum catalyst 1.5Pb$_8$Mn-WMon exhibited an activity 149% more than the manganese-only catalyst in decomposition of H$_2$O$_2$. Evaluation of catalyst stability in the presence of Pb$^{2+}$ after 10 recycles showed only a 6.8% decrease. The catalytic reaction was evaluated based on different criteria.

1. INTRODUCTION

Considering the environmental protection consciousness, hydrogen peroxide as an eco-friendly liquid is used in various industrial processes. These include water and wastewater treatments, the oxygen reduction reaction (ORR) in electrochemical cells, power generation processes, and as an oxidant in industrial processes. These include water and wastewater treatments, the oxygen reduction reaction (ORR) in electrochemical cells, power generation processes, and as an oxidant in industrial processes.1,2 Therefore, catalyzing this reaction improves its efficiency and industrial applications. Over many years, various metals have been used as catalysts and facilitators for this reaction. Among them, manganese with special properties like multivalence capability, nontoxicity, high stability, and structural flexibility is known as a promising catalyst.3

Manganese exists in different valence states of 2+ in MnO$_2$, 3+ in Mn$_2$O$_3$, and 4+ in Mn$_3$O$_4$. Through different states of manganese oxide, MnO$_2$ is the most stable phase, which gives the lowest H$_2$O$_2$ decomposition activation energy ($\sim$50 kJ/mol).5 MnO$_2$ adopts an amorphous or a variety of crystalline forms, depending on the linkage and placement of MnO$_6$ octahedral units.6 The crystalline forms of MnO$_2$ include $\alpha$, $\beta$, $\gamma$, and $\delta$ that are described as $[2 \times 2]$,$[1 \times 1]$, $[1 \times 2]$, and $[1 \times \infty]$ MnO$_6$ unit tunnel structures, respectively. These structural features are nicely discussed in ref 5. Studies on electrode materials indicate that the MnO$_2$ crystalline form controls the oxygen reduction reaction (ORR) and the parallel H$_2$O$_2$ decomposition kinetics in electrochemical cells.6

The most probable mechanism of H$_2$O$_2$ decomposition over the manganese oxide catalyst is briefly described in the following equations.7-9 In the first steps, Mn$^{3+}$ changes to Mn$^{4+}$, and then the catalyst replenishment occurs in the presence of Mn radicals, leading Mn$^{4+}$ to convert to Mn$^{3+}$ (eq 4). Nevertheless, at the beginning of the reaction, due to the low concentration of radicals, the rate of the catalyst replenishment is rather low. To accelerate this, the presence of the optimum concentration of Mn$^{3+}$ species and accelerating the Mn$^{4+}$/Mn$^{3+}$ redox transition in the MnO$_2$ catalyst are crucial.8 Thus, it can easily be concluded that the activity of MnO$_2$ depends on its crystalline form, average oxidation state (AOS), Mn$^{4+}$/Mn$^{3+}$ redox transition ability, particle size, and surface area that are controllable during preparation of catalysts.5,9

$$\begin{align*}
\text{Mn}^{4+} + \text{H}_2\text{O}_2 & \rightarrow \text{H}^+ + \text{HO}_2^- + \text{Mn}^{3+} \\
\text{H}_2\text{O}_2 + \text{HO}_2^- & \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{HO}^* \\
\text{H}_2\text{O}_2 + \text{HO}^* & \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \\
\text{HO}_2^- + \text{Mn}^{3+} & \rightarrow \text{Mn}^{4+} + \text{HO}^- \\
\text{H}^+ + \text{HO}^- & \rightarrow \text{H}_2\text{O}
\end{align*}$$
Table 1. ICP and BET Surface Area Analyses for Different Prepared Catalysts and the Support

| support/catalyst   | ICP (wt %) fresh catalysts | ICP (wt %) used catalysts | surface area (BET) (m^2 g^-1) | pore volume (cm^3 g^-1) | average pore diameter (nm) |
|--------------------|-----------------------------|---------------------------|-------------------------------|------------------------|---------------------------|
| MnO2 monolith      | Mn  | Pb  | Mn  | Pb  | 35.75 | 0.12 | 4.72 |
| wash-coated monolith (WMon) | Mn  | Pb  | Mn  | Pb  | 51.23 | 0.27 | 6.31 |
| 0Pb8Mn-WMon        | 7.27 | 0.94 | 43.72 | 0.23 | 6.74 |
| 0.5Pb8Mn-WMon      | 7.41 | 0.94 | 43.72 | 0.23 | 6.74 |
| 1Pb8Mn-WMon        | 7.65 | 1.33 | 40.16 | 0.21 | 6.95 |
| 1.5Pb8Mn-WMon      | 7.73 | 1.33 | 40.16 | 0.21 | 6.95 |
| 2Pb8Mn-WMon        | 7.68 | 1.33 | 40.16 | 0.21 | 6.95 |
| 2.5Pb8Mn-WMon      | 7.62 | 2.41 | 29.82 | 0.12 | 6.63 |

\[ \text{HO}_2^+ + \text{HO}^+ \rightarrow \text{H}_2\text{O} + \text{O}_2 \] (6)

During \( \text{H}_2\text{O}_2 \) decomposition, because of local pressure and temperature rising, the catalyst undergoes mechanical and thermal shocks, which cause its cracking and active-phase sintering. To avoid the first case, use of macropore monoliths with cordierite composition (2MgO-2Al\(_2\)O\(_3\)-5SiO\(_2\)) has been suggested with regard to high mechanical, thermal, and chemical resistance and low mass transfer limitations.\(^{16}\) Further, to decrease the manganese sintering, the metal surface dispersion or metal–support interaction should be improved. For this aim, aluminum oxide-wash-coated monoliths provide a high surface area with active anchoring sites.\(^{11}\)

Table 1 shows a very low decrease in the metal content, within the experimental errors, confirms the stability of synthesized catalysts.

According to the BET results, wash coating the support increases the surface area, pore volume, and pore diameter that are due to the high surface area of porous alumina, which is established by micro/mesopores.\(^{18}\) By adding manganese, the surface area and pore volume decrease from 51.23 to 27.86 m\(^2\) g\(^{-1}\) for WMon and 0.27 to 0.14 m\(^3\) g\(^{-1}\) for 0Pb8Mn-WMon. This decrease denotes that some pores of the wash-coated layer are blocked by manganese oxide clusters. This is because the surface area of catalysts and pore volume are increased by adding Pb\(^{2+}\), which may be due to the different spreading of Pb\(^{2+}\) and manganese oxide on the wash-coated monolith that prevents manganese oxide-phase sintering and pore blockage.\(^{19}\) This result reflects the structural promoting effect of Pb\(^{2+}\) on the manganese catalyst. Among the prepared catalysts, the 1Pb8Mn-WMon catalyst gives the highest surface area and pore volume. Further, according to the BET results, the average pore diameter increases by loading Pb\(^{2+}\). This can be attributed to the blockage of small pores or forming a new manganese oxide porous layer on the support surface. Thus, the average pore diameter becomes larger than that of the manganese oxide-only catalyst.

The XRD pattern of the lead-free catalyst shows peaks related to MnO\(_2\) and different crystalline phases of MnO\(_2\) marked in Figure 1.\(^{20}\) Since the matrix and the synthesis method of catalysts and the used XRD device were the same for all the samples, the intensity of peaks can be used to make a relative comparison of the phases in the catalysts. By adding Pb\(^{2+}\), the peak intensity of MnO\(_2\) phases increases, while that of MnO\(_3\) decreases. In fact, the decrease of MnO\(_3\) peak intensity is attributed to the structural promoting effect of Pb\(^{2+}\), which causes better manganese dispersion and, in turn, improves the accessibility of the manganese metal to the present surrounding oxygen during preparation and changing the manganese state from MnO\(_3\) to MnO\(_2\).\(^{21}\) Comparing XRD patterns of 0Pb8Mn-WMon and 0.5Pb8Mn-WMon indicates an increase in the \( \alpha \)-MnO\(_2\) peak intensity and the formation of a new Pb\(_x\)Mn\(_{3-x}\)O\(_{16}\) phase (coronadite) where \( x \) is the number of Pb\(^{2+}\), determined by ICP, per the structural formula of Mn\(_{8-x}\)O\(_{16}\) in the prepared catalysts (0.12 < \( x < 0.64\)). Indeed, the Pb\(^{2+}\) template can provide anchoring and nucleation sites for MnO\(_6\) units to form \( \alpha \)-MnO\(_2\) large tunnels during the synthesis, then Pb\(^{2+}\) is absorbed in the \( \alpha \)-MnO\(_2\) tunnel, and the coronadite phase is formed.\(^{14,22}\) The \( \alpha \)-MnO\(_2\) peak intensity increases with Pb\(^{2+}\)
loading up to 1.5 wt % and then decreases, while the intensity of Pb-MnO16 was constant after 1.5 wt %. Further, a new peak at $2\theta = 53.2^\circ$ appears for 1.5Pb8Mn-WMon and 2Pb8Mn-WMon catalysts, which is attributed to the PbO phase according to the X'pert reference database. This matter can happen because (a) almost the entire support surface has been occupied by $\alpha$-MnO2 and there has been no enough space for new $\alpha$-MnO2 tunnels to absorb Pb ions and (b) $\alpha$-MnO2 reaches a maximum capacity of Pb absorption. Under this condition, some of the Pb ions are stable on the surface as a PbO phase, which occupies parts of the support surface and shows an adverse effect on the manganese dispersion. This could increase the probability of manganese agglomeration and thus MnO3 phase formation, which appears in XRD patterns. Further information on the composition of the catalysts was obtained from X-ray photoelectron spectroscopy (XPS) measurements. The XPS spectra of 0Pb8Mn-WMon and 1.5Pb8Mn-WMon reveal the existence of O, Mn, Al, C, and Pb that are marked in Figure 2a,b. Detailed high-resolution XPS of Mn 3s (Figure 2c,d), Mn 2p (Figure 2e,f), and O 1s (Figures 2g,h) was carried out to determine the oxidation state of Mn and the concentration of the oxygen vacancy in the samples.

The AOS of Mn was estimated based on the spectrum of the Mn 3s region and following the formula $AOS = 8.956 - 1.126\Delta E_5$, where $\Delta E_5$ is the binding energy difference between the doublet Mn 3s peaks. The $\Delta E_5$ values of MnO, Mn2O3, and MnO2 are 6.0, 5.5, and 4.7 eV, respectively. The $\Delta E_5$ value determined in the current XPS spectrum was 5.06 eV for 0Pb8Mn-WMon and 4.63 eV for 1.5Pb8Mn-WMon. These data demonstrate that the AOS of Mn changes from 3.26 (in favor of $3+$ oxidation state) to 3.75 (in favor of $4+$ oxidation state) in the presence of Pb2+. The XPS spectra of the Mn 2p peak give rise to a doublet at different binding energies of 641.8 and 653.4 eV, corresponding to the Mn $2p_1/2$ and Mn $2p_1/2$ states. The Mn 2p $1/2$, XPS of 0Pb8Mn-WMon can be fitted by three binding energies of 642.7 eV (correlated with Mn$^{4+}$ in MnO2), 641.3 eV (correlated with Mn$^{4+}$ in MnO2), and 636.8 eV (correlated with Mn$^{3+}$ in MnO) with molar ratios of 35.7, 58.6, and 5.7, respectively. Meanwhile, 1.5Pb8Mn-WMon shows only two peaks at 642.4 and 640.8 eV related to the Mn$^{4+}$ and Mn$^{3+}$ with molar percentages of 67.9 and 32.1%. The AOS of Mn according to the molar ratio of the deconvoluted peak of Mn $2p_1/2$ is 3.3 for 0Pb8Mn-WMon and 3.68 for 1.5Pb8Mn-WMon, which confirms the Mn 3s XPS results as well as XRD results. In fact, manganese decoration by Pb$^{2+}$ can modify the electron density around the metal, change the oxidation state, and increase the abundance of surface Mn$^{3+}$ as an electronic promoter.

The O 1s spectrum is often used to determine the types of surface oxygen species on the oxides. There are three obvious peaks in Figure 2g,h, which correspond to lattice oxygen (Mn–O–Mn) (O), defect oxygen (Mn–O–H) (O$^\delta$), and surface-adsorbed water molecules (H–O–H) (O$^\delta$)'s whose structures are nicely shown in Figure 3. For the samples, binding energies of $529.7-530.1$, $531.2-531.8$, and $532.4-533.2$ eV are attributed to O$^\omega$, O$^\delta$, and O$^\delta$,$^\delta$, respectively. The oxygen distribution percentage, reported in Table 2, demonstrates that 1.5Pb8Mn-WMon contains the most abundant defect oxygen and also oxygen vacancies because water molecules are usually adsorbed at the oxygen vacancies of an oxide material. As was reported in the XRD patterns, the presence of Pb$^{2+}$ supports the formation of $\alpha$-MnO2 and Pb$_x$Mn$_{16}$O$_{16}$ phases. Pb$_x$Mn$_{16}$O$_{16}$ maintains neutral charge by forming Mn$^{3+}$/Mn$^{4+}$, Pb$^{2+}$/Pb$^{3+}$, Mn$^{4+}$/Pb$^{2+}$, and Mn$^{3+}$/Pb$^{3+}$ redox couples and generates the optimal electron availability and electron mobility at the surface that accelerates the Mn$^{3+}$/Mn$^{4+}$ transition and increases the oxygen vacancy.

Thermogravimetric analysis (TGA) was performed to determine thermal stability of the products. The obtained TGA profile (Figure 3) can be divided into three temperature zones: at temperatures below 200 °C, dehydration of physically adsorbed surface water occurs; at temperatures within 200–480 °C, the chemisorbed water in the tunnel structure of MnO2 is removed, and at temperatures higher than 500 °C, the material undergoes decomposition to form MnO2 and then MnO2 (MnO2 $\rightarrow$ MnO$_2$, which is assigned to the release of the MnO2 lattice oxygen and complete transformation into MnO$_2$. The amount of surface-adsorbed water in these samples was from 1.15 to 2.2 wt % (Figure 3). In fact, adding Pb$^{2+}$ to the manganese catalyst increases the surface area and the amount of surface-adsorbed water. On the other hand, according to the XPS result, the amounts of oxygen vacancies and the water molecules that are usually absorbed at the oxygen vacancies increase, and consequently the TGA mass loss increases. The lead-free sample showed the highest amount of tunnel water content of 1.53 wt %. In the absence of Pb$^{2+}$, more vacant tunnel sites are available for water to stabilize the structure and balance the charge. Compared to the lead-free catalyst, the peaks corresponding to the MnO2 transition to MnO3 shift to higher temperatures, indicating that the lattice oxygen in the Pb$_x$Mn$_{16}$O$_{16}$ phase is more stable after Pb$^{2+}$ cations reside in $\alpha$-MnO2. Meanwhile, the mass loss percentage related to the phase transition increases in the presence of Pb$^{2+}$.

Figure 4 shows the TPR spectra of the prepared catalysts. For the lead-free (0Pb8Mn-WMon) catalyst, two main peaks are observed. The first at 324 °C with a shoulder at 375 °C is typically assigned to the reduction of MnO2 to MnO$\delta$.$^\delta$. This peak also includes the reduction of transition-state MnO3, which appears like a shoulder at higher temperatures. The second peak at 496 °C is typically due to reduction of MnO2 to MnO. As shown in Figure 4, by adding the Pb$^{2+}$ template and transfer of the $\beta$-$\mathrm{MnO}_2$ phase to $\alpha$-$\mathrm{MnO}_2$, according to XRD results, the reduction temperature decreases, and catalyst reducibility increases. This electronic promoting effect of Pb$^{2+}$ occurs due to the existence of abundant mobile surface oxygen species in $\alpha$-$\mathrm{MnO}_2$ structures that are identified in the XPS spectra. Also, the shoulder of the first appearing peak is related to MnO$_2$ phase reduction that has a significant decrease in H$_2$. 

Figure 1. XRD patterns of the different prepared catalysts.
uptake up to 1 wt % Pb\textsuperscript{2+} loading and then tends to increase, consistent with XRD patterns. The total H\textsubscript{2} consumption for reduction steps (appropriate to the surface area under each curve) is found to have the maximum value at 1.5 wt % Pb\textsuperscript{2+}, corresponding to the higher number of active sites with this amount of Pb\textsuperscript{2+}. TPR spectra of 2Pb\textsubscript{8}Mn-WMon show a broad peak at 324 °C due to the probable PbO formation, and the phase reduction peaks overlap.\textsuperscript{34}

The results of TPD analysis, presented in Table 3, depict the metal dispersion and the crystallite average size. The results indicate that adding Pb\textsuperscript{2+} to the manganese catalyst increases the hydrogen uptake, metal dispersion on the surface, and the

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**Figure 2.** XPS spectra of (a) 0Pb\textsubscript{8}Mn-WMon and (b) 1.5Pb\textsubscript{8}Mn-WMon catalysts; Mn 3s spectra for (c) 0Pb\textsubscript{8}Mn-WMon and (d) 1.5Pb\textsubscript{8}Mn-WMon, Mn 2p spectra for (e) 0Pb\textsubscript{8}Mn-WMon and (f) 1.5Pb\textsubscript{8}Mn-WMon, and O 1s spectra for (g) 0Pb\textsubscript{8}Mn-WMon and (h) 1.5Pb\textsubscript{8}Mn-WMon.
number of the manganese oxide crystallites, which is in accordance with the TPR results. This trend continued up to 1.5 wt % Pb\textsuperscript{2+} loading but stopped for an excess amount. Thus, it implies that Pb\textsuperscript{2+} by enhancing the MnO\textsubscript{2} dispersion provides space and anchoring sites for crystal growth and forms α-MnO\textsubscript{2} large tunnels as well as the coronadite phase. Higher dispersions and smaller MnO\textsubscript{2} crystallite sizes in the presence of Pb\textsuperscript{2+} will increase the number of accessible active sites for H\textsubscript{2}O\textsubscript{2} decomposition.

The FESEM images and EDX patterns of 0Pb\textsubscript{8}Mn-WMon as well as the 1.5Pb\textsubscript{8}Mn-WMon catalyst are shown in Figure 5. Catalysts show different morphologies as cubic and spherical aggregates of nanoparticles. SEM images in Figure 5a,b reveal that the Pb\textsuperscript{2+}-loaded samples provide a better dispersion, lower average size, and a porous layer on the wash-coated monolith surface. To further explore the manganese distribution on the support surface, elemental mapping analysis by FESEM was performed. Figure 5c,d shows that the manganese in the 1.5Pb\textsubscript{8}Mn-WMon catalyst was distributed more uniformly. Spectra obtained from EDX (Figure 5e,f) verified that 0Pb\textsubscript{8}Mn-

\begin{table}[h]
\centering
\caption{Summary of XPS Data of 0Pb\textsubscript{8}Mn-WMon and 1.5Pb\textsubscript{8}Mn-WMon Catalysts}
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\textbf{catalyst} & \textbf{\(\Delta E_s\) (eV)} & \textbf{AOS} & \textbf{molar percentage (%)} & \textbf{oxygen distribution (%)} \\
0Pb\textsubscript{8}Mn-WMon & 5.06 & 3.3 & 35.7 & 74.1 & 25.9 \\
1.5Pb\textsubscript{8}Mn-WMon & 4.63 & 3.68 & 67.9 & 52.7 & 33.1 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Crystallite Size of Manganese Particles Determined by H\textsubscript{2} Chemisorption}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{catalyst} & \textbf{\(D\) (%)} & \textbf{active sites no. \((\times 10^{20})\) \((g^{-1} \text{cat})\)} \\
0Pb\textsubscript{8}Mn-WMon & 17.97 & 1.63 \\
0.5Pb\textsubscript{8}Mn-WMon & 23.02 & 2.09 \\
1Pb\textsubscript{8}Mn-WMon & 27.09 & 2.46 \\
1.5Pb\textsubscript{8}Mn-WMon & 29.23 & 2.65 \\
2Pb\textsubscript{8}Mn-WMon & 25.66 & 2.33 \\
\hline
\end{tabular}
\end{table}
WMon was made up of 50.27% Mn and 26.22% Al, Si, and Mg, with a mass ratio of Mn/O equal to 2.03, while 1.5Pb8Mn-WMon was made up of 57.69% Mn, 6.12% Pb, and 5.01% Al, Si, and Mg, with a mass ratio of Mn/O of 1.85. In fact, enormous MnO2 was formed at the surface in the presence of Pb2+. The TEM images (Figure 6 a,b) of 0Pb8Mn-WMon and 1.5Pb8Mn-WMon catalysts show remarkably uniform dispersion of manganese oxide crystals on the monolith surface that is more obvious for the latter sample. HRTEM images were also used to detect the interplanar d spacing data of the MnO2 crystalline structure. In Figure 6c, the lattice fringes correspond to d spacings of 0.31 and 0.69 nm, characteristics of β-MnO2 (110) and α-MnO2 (110) facets, respectively.6,14,36 These results are in agreement with the XRD pattern for the 0Pb8Mn-WMon catalyst. Also, in some zones, crystal aggregation is observed. Meanwhile, HRTEM image of the 1.5Pb8Mn-WMon catalyst (Figure 6d) shows a smooth texture with one dominant crystalline form. In this catalyst, the interplanar d spacing values in some zones was estimated to be (~0.75 nm), while the interplanar d spacing value for the α-MnO2 (110) facet was 0.69 nm from observations in the HRTEM image of the lead-free sample. Thus, it is highly possible that the host α-MnO2 tunnel extraction occurs due to the Pb2+ occupation since the dimension of the tunnels in α-MnO2 is sufficiently extensive to embed a guest ion.37

2.2. Activity and Stability Analysis. The performance of a manganese catalyst is related to the crystalline form of manganese, the available surface active sites, the manganese ability to interchange oxidation states (Mn3+/Mn4+), the manganese dispersion percentage, and metal oxide reducibility.38 Here, the prepared Pb2+-loaded and the manganese-only catalyst performance was evaluated in the experimental setup under atmospheric pressure and a 5 mL (70%) hydrogen peroxide injection. The temperature was raised and maintained at 40 ± 3 °C by the cooling water flow. Data were obtained and expressed in terms of H2O2 conversion (X), reaction constant rate (k), turn over frequency (TOF), and turn over number (TON).38

H2O2 conversion () was calculated by the O2 mole ratio determined from the rejected water monitored by a digital scale () to the O2 mole if hydrogen peroxide was completely decomposed ().39 The ideal gas law was used to calculate the number of released O2 moles. Here, p is the atmospheric pressure, V is the released O2 volume, R is the ideal gas constant, and T is ambient temperature. Thus,

\[
X_{\text{H}_2\text{O}_2} = 1 - \frac{n_{\text{H}_2\text{O}_2}}{n_{\text{O}_2}} = \frac{n_{\text{H}_2\text{O}_2}}{n_{\text{O}_2}}
\]

(7)

Results indicate that H2O2 decomposition over manganese behaves as a pseudo-first-order reaction for 30 s, and the reaction rate constant (k) can be expressed as

\[
\ln \frac{n_{\text{H}_2\text{O}_2}}{n_{\text{O}_2}} = -kt
\]

(8)
Figure 6. TEM and HRTEM images of (a, c) the 0Pb8Mn-WMon and (b, d) the 1.5Pb8Mn-WMon samples.

Figure 7. $\text{H}_2\text{O}_2$ conversion versus time for different catalyst loadings of Pb$^{2+}$.
In eqs 7 and 8, is the present mole of H$_2$O$_2$ in the solution at time $t$ and is the initial mole of H$_2$O$_2$.

The turnover frequency (TOF) can be determined per mole of metal, but the turnover number (TON) should be calculated per metal active site according to the following equations:

$$
\text{TOF} = \frac{n_0 - n_t}{t \times n_{\text{metal}}} = \frac{(n_0 - n_t)_H_2O_2}{t \times n_{\text{metal}}} = \frac{2n_{(O)} }{t \times n_{\text{metal}}} = \frac{2n_{(O)} }{n_{\text{metal}}} \times \frac{1}{RT}
$$

$$
\text{TON} = \frac{n_0 - n_t}{t \times N_{\text{Ac}}} = \frac{(n_0 - n_t)_H_2O_2 \times N_{\text{Ac}}}{t \times N_{\text{Ac}}} = \frac{2n_{(O)} }{t \times N_{\text{Ac}}} \times N_{\text{Ac}}
$$

where $n_{\text{metal}}$ and $N_{\text{Ac}}$ are the moles of metal and the number of metal active sites on the catalyst, respectively.

Figure 7 shows decomposition conversion of 5 mL of H$_2$O$_2$ in the presence of different catalyst loadings of Pb$^{2+}$. The reaction rates are evidenced by the slopes of their H$_2$O$_2$ conversion over time curves. Figure 8 shows the H$_2$O$_2$ decomposition conversion of catalysts after 10, 20, 30, and 40 s using different prepared catalysts. The activity of the manganese catalyst is remarkably promoted in the presence of the Pb$^{2+}$ template. The highest catalytic activity and almost complete conversion were achieved with the 1.5Pb$_8$Mn-WMon catalyst where 149% enhancement in conversion (compared to only manganese catalyst) was achieved after 30 s and a rather complete decomposition after 40 s.

Table 4 presents the H$_2$O$_2$ conversion and the reaction rate constant ($k$), turnover frequency (TOF), and turnover number (TON) for different used catalysts after 30 s.

| Parameter          | 0Pb8Mn-WMon | 0.5Pb8Mn-WMon | 1Pb8Mn-WMon | 1.5Pb8Mn-WMon | 2Pb8Mn-WMon | 2.5Pb8Mn-WMon |
|--------------------|-------------|---------------|-------------|---------------|-------------|---------------|
| $k \times 10^{-2}$ (s$^{-1}$) | 0.371       | 0.498         | 0.643       | 0.924         | 0.801       | 0.482         |
| TOF $\times 10^2$ | 1.62        | 2.19          | 2.86        | 4.08          | 3.52        | 2.04          |
| TON $\times 10^2$ | 9.04        | 9.55          | 11.27       | 13.98         | 13.01       |               |

Figure 8. H$_2$O$_2$ conversion versus different loadings of Pb$^{2+}$ at different times.

Table 4. H$_2$O$_2$ Conversion, Reaction Rate Constant ($k$), Turn Over Frequency (TOF), and Turn Over Number (TON) for Different Used Catalysts after 30 s

In eqs 7 and 8, is the present mole of H$_2$O$_2$ in the solution at time $t$ and is the initial mole of H$_2$O$_2$.

The turnover frequency (TOF) can be determined per mole of metal, but the turnover number (TON) should be calculated per metal active site according to the following equations:

$$
\text{TOF} = \frac{n_0 - n_t}{t \times n_{\text{metal}}} = \frac{(n_0 - n_t)_H_2O_2}{t \times n_{\text{metal}}} = \frac{2n_{(O)} }{t \times n_{\text{metal}}} = \frac{2n_{(O)} }{n_{\text{metal}}} \times \frac{1}{RT}
$$

$$
\text{TON} = \frac{n_0 - n_t}{t \times N_{\text{Ac}}} = \frac{(n_0 - n_t)_H_2O_2 \times N_{\text{Ac}}}{t \times N_{\text{Ac}}} = \frac{2n_{(O)} }{t \times N_{\text{Ac}}} \times N_{\text{Ac}}
$$

where $n_{\text{metal}}$ and $N_{\text{Ac}}$ are the moles of metal and the number of metal active sites on the catalyst, respectively.

First of all, the higher metal dispersion and the more active sites on the catalyst surface increase the H$_2$O$_2$ accessibility to the reaction sites. However, if the number of active sites was the only influencing factor, the 1Pb$_8$Mn-WMon catalyst would exhibit a greater $k$ value than 2Pb$_8$Mn-WMon based on the TPR and H$_2$ chemisorption results; however, it was not. Thus, the other promotional effect of Pb$^{2+}$, that is, transformation of Mn$_2$O$_3$ into the MnO$_2$ phase, appearing in XRD, XPS and EDX patterns, was relevant. According to the XRD patterns, the minimum Mn$_2$O$_3$ phase ratio was relevant to 1Pb$_8$Mn-WMon, but its activity still appeared to be less than that of 1.5Pb$_8$Mn-WMon. In this regard, apparently, the role of Pb$^{2+}$ in increasing the surface $\alpha$-MnO$_2$ and the Pb$_x$Mn$_8$O$_{16}$ phase formation, which is reflected by TON and TOF values, is principal.

As shown in Table 4, the 1.5Pb$_8$Mn-WMon catalyst with the highest ratio of $\alpha$-MnO$_2$ and Pb$_x$Mn$_8$O$_{16}$ phases exhibits the maximum TON value. Comparing the 1.5Pb$_8$Mn-WMon and 2Pb$_8$Mn-WMon catalysts with approximately the same quantity of Pb$_x$Mn$_8$O$_{16}$ shows that the TON value is slightly lower for 2Pb$_8$Mn-WMon, despite a lower $\alpha$-MnO$_2$ quantity and a higher Mn$_2$O$_3$ phase. This observation specifies the more important role of Pb$_x$Mn$_8$O$_{16}$ in the catalyst activity.

Regarding the $\alpha$-MnO$_2$ phase, the increase of Mn–O–H groups on the catalyst surface (according to the XPS results) improves the manganese reducibility (TPR analysis) and the Mn$^{4+}$ to Mn$^{3+}$ transition, which accelerates the H$_2$O$_2$ adsorption on the catalyst surface. Also, regarding Pb$_{x}$Mn$_n$O$_{16}$ in which Pb$^{2+}$ resides in the $\alpha$-MnO$_2$ tunnel and maintains neutral charge by forming Mn$^{3+}$/Mn$^{4+}$, Pb$^{2+}$/Pb$^{3+}$, Mn$^{4+}$/Pb$^{2+}$, and Mn$^{3+}$/Pb$^{3+}$ redox couples, the optimal electron availability and electron
mobility at the catalyst surface is provided, which increases the oxygen vacancy (localized Mn$^{3+}$) in the structure and accelerates the Mn$^{3+}$ to Mn$^{4+}$ transition.\textsuperscript{29}

The stability of 0Pb8Mn-WMon and 1.5Pb8Mn-WMon catalysts is typically compared in Figure 9, for 10 usage cycles and after 30 s of reactions. For the 1.5Pb8Mn-WMon catalyst, the H$_2$O$_2$ conversion decreased from 92.3 to 86.4 (6.4% decrease), whereas for the 0Pb8Mn-WMon catalyst, the H$_2$O$_2$ conversion decreased from 37.1 to 17.6 (52.5% decrease). The decrease of catalytic activity could be attributed to the active site agglomeration and active site occupation with the intermediates that change the balance of Mn$^{3+}$ and Mn$^{4+}$ on the MnO$_2$ crystalline surface.\textsuperscript{41,42} Based on the structural characterization results, the 1.5Pb8Mn-WMon catalyst exhibits the best metallic dispersions and the smallest particle size. Smaller active sites make a stronger interaction with the support surface and provide anchoring sites, which can reduce the catalyst mass loss during reaction and decrease the non-favorable metal site agglomeration.\textsuperscript{41} Also, the 1.5Pb8Mn-WMon catalyst with a higher number of oxygen defects and oxygen vacancies (localized Mn$^{3+}$) could postpone the active site occupation and Mn$^{3+}$ and Mn$^{4+}$ balance changes and could improve the catalyst replenishment.\textsuperscript{42,43}

2.3. Proposed Mechanism for Hydrogen Peroxide Decomposition. As was presented in the structural characterization, adding the Pb$^{2+}$ template to the manganese catalyst increases the AOS and the amount of α-MnO$_2$ phase. Also, the higher number of oxygen vacancies and defect oxygens was observed in 1.5Pb8Mn-WMon, which is due to the unique crystalline structure of α-MnO$_2$ and Pb$_x$Mn$_{8}$O$_{16}$ that could maintain the neutral charge in the presence of oxygen vacancies. Meanwhile, the hydrogen peroxide decomposition is controlled by the catalyst oxidation state, but the catalyst activity investigation together with characterization showed that the surface chemistry is the dominant phenomenon. Thus, the most important parameters to control the H$_2$O$_2$ decomposition are the oxygen vacancy (localized on Mn$^{3+}$) and defect oxygen (Mn−O−H groups).\textsuperscript{31,44} The oxygen vacancy facilitates the H$_2$O$_2$ adsorption and the O−O bond dissociation to form two surface bound hydroxyl radicals (HO·). Meanwhile, at the defect oxygen sites, the adsorbed H$_2$O$_2$ molecules can provide hydrogen transfer to the O−H group of Mn−O−H, and a H$_2$O molecule will be produced as well as a surface bound

![Figure 9](image-url) Stability of 0Pb8Mn-WMon and 1.5Pb8Mn-WMon catalysts in recycles after 30 s reaction time.

![Figure 10](image-url) Schematic of hydrogen peroxide decomposition on the prepared catalyst.
hydroperoxyl radical (HOO·) from which H₂O and O₂ molecules will be generated in the reaction with another adsorbed H₂O₂ molecule or with a hydroxyl group. Based on these, the H₂O₂ decomposition steps on the MnO₂ surface are depicted in detail in Figure 10.

3. CONCLUSIONS

This study explored that the presence of Pb²⁺ promotes the structural and electronic properties of the manganese oxide catalyst. The H₂O₂ decomposition activity of a monolithic supported MnO₂ catalyst reaches a maximum at 1.5 wt % Pb²⁺ loading. According to the physicochemical characterization, incorporating Pb²⁺ templates into the manganese catalyst improves the manganese dispersion, decreases the average particles size and the number of blocked pores, and supports the formation of an active α-MnO₂ phase. Better dispersion changes the oxidation state from Mn₂O₃ to MnO₂ by modifying the metal accessibility to the surface oxygen species. The most outstanding effect was the formation of a new Pb₃Mn₉O₁₆ phase, which increases thermal stability of α-MnO₂ and favors the redox decomposition process due to electron transfers in Mn⁴⁺/Mn³⁺, Pb²⁺/Pb³⁺, and Mn⁴⁺/Pb²⁺ couples, leading the oxygen vacancies to appear at the surface. The new structural defects and the surface oxygen vacancies accelerate the H₂O₂ adsorption and greatly improve the reaction rate as well as the TOF and TON criteria. The presence of Pb²⁺ was also relevant to much higher catalytic stability.

4. EXPERIMENTAL SECTION

4.1. Materials. Square channel cordierite monoliths, as the support for the catalysts, were supplied by Delco Co. The cylindrical monolith pieces had dimensions of 1 cm diameter and 0.5 cm length. The support structure contained 600 cells per in.², and the specific surface area was 37.6 m² g⁻¹. For making the wash-coat layer, the used γ alumina (BET = 190 m² g⁻¹, 99%) and α-alumina powders (BET = 13 m² g⁻¹, 99%) were the products of US Research Nanomaterials, Inc. Poly(vinyl alcohol) (PVA, 98%) for dispersing powders and Mn(NO₃)₂·4H₂O (99.0%) and Pb(NO₃)₂ (≥99.0%) for the catalyst synthesis were also Merck products. H₂O₂ solution (70%) was a Degussa AG product. Deionized water was used for preparing solutions throughout the experiments.

4.2. Methods. 4.2.1. Catalyst Preparation. For preparing the xPhyMn-WMon product, the xPhyMn catalyst was synthesized over the wash-coated cordierite monolith support. Different composite catalysts were prepared with different Pb²⁺ loadings of 0, 0.5, 1.0, 1.5, 2, and 2.5 wt %, while a constant Mn loading of 8 wt % was used for providing a nearly monolayer of Mn on the support. Before catalyst preparation, the support was dried at 120 °C in a vacuum oven overnight to eliminate impurities and humidity. To increase the surface area of the monoliths and provide a chemically active anchoring site for metal particles, the monoliths were coated by dipping into stock aqueous suspensions of alumina prepared by dispersing γ and α alumina powders and PVA with a 1.5:1:1 mass ratio in 25 mL of deionized water. Stirring the mixture overnight gave a homogeneous suspension. To achieve good adhesion of the Al₂O₃ layer on the monolith substrate, 90% of the alumina powder diameters were less than 4 μm. In this way, the surface of the square channel monoliths was fully covered by a layer of precursor, and then the support was withdrawn from the stock suspension. After that, the support was dried at 90 °C for 6 h in a vacuum oven and calcined at 700 °C for 3 h with a heating rate of 3 °C min⁻¹ to eliminate the binder and impurities in a furnace.

The catalysts were prepared by sequential impregnation of the support in solutions with specified concentrations of Mn(NO₃)₂ and Pb(NO₃)₂. After impregnation, the products were dried at 90 °C in a vacuum oven for 10 h and then were calcined at 450 °C for 3 h, with a heating rate of 3 °C min⁻¹ in a furnace. The weight of each catalyst piece was ~200 mg. Figure 11 illustrates the different steps of the catalyst preparation.

4.2.2. Characterization of Catalysts. The weight percentages of Mn and Pb metals, deposited on the monolith surface, were measured by the inductively coupled plasma (ICP) method using a Varian VISTA-MPX CCD simultaneous instrument. The BET area, pore volume, and average pore size of the support and prepared catalysts were determined by the BET surface area and BJH pore size distribution measurements using a Micromeritics ASAP-2010 system. A Philips analytical X-ray diffractometer (XPERTMPD) with monochromatized Cu Kα was used to record the X-ray
diffraction (XRD) patterns of the catalysts. Using the XRD pattern, the different formed metal phases were identified. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo Scientific K-Alpha system. The spectrometer was equipped with a high-resolution Al Kα X-ray monochromator. The XPS spectra were recorded under a source energy between 0 and 800 eV with reference to the C 1s peak (285.6 eV). Thermogravimetric analysis (TGA) was carried out by means of a Linneys STA-1600 apparatus under air flow in a temperature range of 25−1000 °C at a rate of 10 °C min−1.

The hydrogen temperature-programmed reduction (H₂-TPR) analysis was performed using a Micrometrics TPD−TPR 2900 system equipped with a thermal conductivity detector (TCD). First, trace amounts of water and gases were removed from the catalysts under a helium atmosphere at 140 °C. After cooling the catalysts, TPR of samples was obtained in a stream of hydrogen under atmospheric pressure and a linearly programmed heating of 10 °C min−1 up to 700 °C. The amounts of chemisorbed hydrogen on the catalysts were also measured. First, the catalyst was reduced under a hydrogen atmosphere, and then the flow of hydrogen was switched to argon gas to remove the physisorbed hydrogen. Afterward, temperature-programmed desorption (TPD) of the samples was performed by increasing the temperature. The data were used to calculate the metal dispersion, average crystallite size, and number of crystallites per catalyst mass according to the following equations:

\[ D(\%) = \frac{N_s}{N_t} \times 100 \]  
\[ d_{VA} = \frac{\nu_m/a_m}{D} \]  
\[ N_{AC} = \frac{wt \times D \times N_A}{100 \times M} \]

where \( D \) is the dispersion percentage of manganese, \( N_s \) is the number of surface atoms, \( N_t \) is the total number of atoms in the bulk and on the surface, \( d_{VA} \) is the volume-area mean particle size, \( \nu_m \) is the volume of an atom, and \( a_m \) is the area occupied by a surface atom. Also, \( N_A \) is the number of active surface sites, \( wt \) is the manganese weight per each gram of catalyst (0.08), \( M \) is the molar weight of manganese, and \( N_A \) is the Avogadro number.

Finally, the morphology of catalysts was observed through field emission scanning electron microscopy (FESEM, MIRA3 Tescan), energy-dispersive X-ray spectroscopy (EDX, MIRA3 Tescan at 20 kV), and high-resolution transmission electron microscopy (HRTEM, Philips Tecnai G2 F20) images.

4.2.3. Experimental Setup. An experimental setup in which a sample of cylindrical monolith base was coated with a catalyst was used to examine the hydrogen peroxide decomposition by monitoring the changes in temperature and \( \text{O}_2 \) production over time. The setup was made of three main sections (Figure 12):

- The injection part comprised a delivery tank for holding the hydrogen peroxide and a solenoid valve. A nitrogen supply was used to force the hydrogen peroxide through the solenoid valve into the vessel. The delivery tank was pressurized with nitrogen to a constant pressure to ensure the complete injection of the hydrogen peroxide. It was thought that the decomposition products, generated by a very reactive catalyst, might cause a local increase in pressure. Then, the injection pressure should be high enough to enter the hydrogen peroxide impulsively into the decomposition vessel.

- The reaction chamber was made of stainless steel with an inner diameter of 50 mm and an internal height of 70 mm that can withstand high-pressure and high-temperature conditions. A small vessel with an internal diameter of 15 mm and a length of 55 mm was embedded in the center of the reactor. First, a piece of prepared catalyst was loaded (accurately weighted), then concentrated \( \text{H}_2\text{O}_2 \) was injected, and the gas products were conducted toward the exit line. A pod was fixed close to the decomposition vessel to measure the temperature using a K-type thermocouple. All reactions were conducted at a temperature of 40 ± 3 °C via a controlled cooling water flow in the provided jacket around the decomposition vessel. To

![Figure 12. Schematic illustration of the used setup for \( \text{H}_2\text{O}_2 \) catalytic decomposition.](image-url)
ensure compatibility with hydrogen peroxide and its products, the whole assembly was manufactured with stainless steel grade 316.

- In the analyzing section, the generated gas came out from the reactor through a brine solution trap for the separation of H2O and non-converted H2O2, and the released oxygen was conducted to a water-containing Erlenmeyer flask where a connection from water to another atmospheric pressure Erlenmeyer flask was provided and any excess pressure would provide a flow of water to this Erlenmeyer flask, which was placed on a 0.001 g digital balance to measure the received water due to the oxygen production. In this way, H2O2 decomposition was monitored with time.

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