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Oxygen Scavenging Hybrid Nanostructure: Localization of Different Iron Nanoparticles on Montmorillonite Clays Host

Khadijeh Khederlou, Reza Bagheri, Akbar Shojaei, Nathalie Gontard, and Yousef Tamsilian

ABSTRACT: According to the great potential of zero-valent iron nanoparticle applications in the environmental, medical, chemical, packaging and many other industries, there is still a need to tailor their production methods. This study reports the production of a hybrid nanostructure based on iron nanoparticles (INPs) produced in/on montmorillonite (MMT) nanoclays as an oxygen scavenger and barrier additive in polymeric packaging materials of oxygen-sensitive products. INPs and MMT were demonstrated to have effective mutual interactions in which the MMT host played a chemophysical trapping role for iron particles, causing smaller particles around 10 nm with 6.2 g/m² higher specific surface area by limiting particle growth and agglomeration. In return, the embedding of primary iron cations in/on clays and growth of these particles during the reduction reaction pushed the clay layers out and helped further clay intercalation–exfoliation. Effective study of solvent and primary cation (Fe²⁺/Fe³⁺) types showed different preferences in interacting with natural and alkylammonium-modified MMT, resulting in the different site selection. Fe³⁺ cations preferred to migrate to the interlayer space, whereas Fe²⁺ cations tended to bond to the clay surface. The obtained results in this study suggest tailoring the ultimate oxygen scavenging capacity, shelf life, and migration properties of a hybrid nanoparticle according to the application requirements.

1. INTRODUCTION

Highly reactive zero-valent iron nanoparticles (ZVINPs) are some of the most important synthetic nanoparticles due to their high specific surface area, strong reducing power, and bio-compatible properties which enable them to have many potential applications such as environmental (e.g., soil remediation, groundwater decontamination, water purification), biomedical (e.g., imaging or targeted anticancer therapy), and food contact materials (e.g., active and intelligent packaging). Researchers report excellent uptake mechanisms for the food degradation supports the idea of an oxygen absorption system in which to imbed polymeric materials.

Iron nanoparticles with an average diameter of 110 nm have been studied as oxygen scavengers to prevent lipid oxidation of roasted sunflower seeds and walnuts. The scavenger capacity was almost 10 times greater than that of conventional iron powders. On the nanoscale, the specific surface area of iron particles is 30 times more than micron size. Most of the reported ZVINP sizes produced by different research groups are 100–200 nm, and just a few groups reported the ZVINP were produced in a size below 30 nm.

Over the years, the classic borohydride reduction method for preparing ZVINPs has been modified using various stabilizers or surface modifiers to acquire more stable and appropriate ZVINP delivery for scavenging gaseous oxygen, treating different organic and inorganic contaminants in water and soil, and targeting drug delivery and improved magnetic resonance imaging.

Reducing an aqueous iron salt in the presence of a support material can reduce the effect of iron nanoparticle aggregation,
offering a higher specific surface area and consequently a higher reactivity.\textsuperscript{19,28,39} A number of researchers have attempted to anchor iron nanoparticles on solid supports such as zeolites,\textsuperscript{40–43} graphene and active carbons,\textsuperscript{10,12,44,45} and nanoclays.\textsuperscript{46–52} This strategy provides several advantages like surpassing the aggregation of zero-valent iron nanoparticles and protecting particles from the oxidation to more easily disperse in a polymer matrix for further applications.

In recent years, among all potential supports, nanoclays have attracted considerable interest as an iron particle support due to their high specific surface area and unusual intercalation properties. Eliminating microbes, anions, and hazardous compounds,\textsuperscript{1,53,54} immobilizing the enzymes,\textsuperscript{5} and preparing conductive nanocomposites\textsuperscript{55} are some productive targets of this work is to explore new pathways of INP production and to develop additional knowledge to modulate INP reactivity for optimizing the oxygen scavenging capability of iron-based active systems in food packaging materials. The ultimate objective is to investigate INP preparation conditions and to clarify the position of INP produced from different iron cations (Fe\textsuperscript{2+}/Fe\textsuperscript{3+}) located on MMT supports.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

Natural montmorillonite (CNa\textsuperscript{+}), organically modified montmorillonite with dimethyl dehydrogenated tallow and quaternary ammonium (C20A), was supplied by Southern Clay Products Inc. (Texas, USA). Two different iron salts, FeCl\textsubscript{3}·6H\textsubscript{2}O and FeCl\textsubscript{2}·6H\textsubscript{2}O, sodium borohydride (NaBH\textsubscript{4}, 99%), ethanol (C\textsubscript{2}H\textsubscript{5}OH, EtOH, 99.8%), and sodium hydroxide solution (NaOH, 97%) were obtained from Sigma-Aldrich (France).

#### 2.2. Preparation of Compounds

<table>
<thead>
<tr>
<th>Table 1. Formulation of Prepared INP-Imbedded MMT Clay and Zero-Valent Iron Nanoparticle Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INP-imbedded MMT clay</strong></td>
</tr>
<tr>
<td>solution</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
<tr>
<td>NaBH\textsubscript{4}</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{5}OH</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
</tr>
<tr>
<td>FeCl\textsubscript{2}·4H\textsubscript{2}O</td>
</tr>
<tr>
<td>FeCl\textsubscript{3}·6H\textsubscript{2}O</td>
</tr>
<tr>
<td>C20A</td>
</tr>
<tr>
<td>CNa\textsuperscript{+}</td>
</tr>
</tbody>
</table>

Despite the similar initial \(d\) value of clay platelets in kaolinite and MMT, the surface charge and cation exchange capacity (CEC) in kaolinite (3−15 × 10\textsuperscript{-5} equiv/g) is much lower than that of MMT (80−100 × 10\textsuperscript{-5} equiv/g).\textsuperscript{58} This small ion exchange capacity initiated from H-bonding interlayer forces makes it difficult to seek good results to increase the \(d\) value between platelets modified by alkylammonium ion. Hence, kaolinite has poor dispersion results in hydrophobic matrixes.\textsuperscript{59}

On the other hand, normally, the specific surface area of kaolinite is less than MMT depending on the ordering of these clays.\textsuperscript{46} MMT is a naturally 2:1-type layered aluminosilicate with a turbostratic structure,\textsuperscript{60} where each layer comprises an alumina octahedral sheet sandwiched between two silicate tetrahedral sheets, and the layer has a permanent negative charge resulting from isomorphous substitution occurring mainly in the octahedral sheet. Such layers are stacked by weak dipolar or van der Waals forces, leading to the intercalation of charge-compensating cations into the interlayer space and causing MMT to be easily expanded along the \(c\)-direction. Therefore, not only adsorption of target components on the external surface but also introduction of these components into the interlayer space can occur.\textsuperscript{46}

Surveying advantages of MMT and embedding INP in the polymeric materials for the oxygen scavenging system, the main purpose of this work is to explore new pathways of INP production and to develop additional knowledge to modulate
freeze-dryer (Christ Alpha 2-4 LSC, Osterode, Germany) at \(-100^\circ\text{C}\) and 0.3 mbar overnight. To compare, Fe\(^0\) (ZVINPs), was produced from Fe\(^{2+}\) and Fe\(^{3+}\) cations with the same process in the absence of clay. Considering that the surface charge of CNa\(^+\) originated from OH groups and the polarity of C20A, it was hypothesized that polar solvent having OH groups such as ethanol could facilitate the clay dispersion compared to conventionally used aqueous solution. The ethanol/water ratio of 4:1 (v/v) was selected as the dispersing solvent, having enough water for the Fe cations for the reduction reaction to ZVINPs. Moreover, as the hydrogen ions were responsible for the ZVINP resolubilization, a small amount of sodium hydroxide, NaOH, was added to the borohydride reducing solution to neutralize H\(^+\) ions. Figure 1 shows the production procedure schematic of the iron nanoparticle embedded in the MMT clay.

2.3. Characterization and Measurement. X-ray diffraction (XRD) patterns from samples were obtained using a PANalytical X’Pert diffractometer (Malvern Panalytical Ltd., Malvern, UK) with Cu K\(\alpha\) radiation (\(\lambda = 1.54\) Å) in the reflection mode. The average diameter size of the resulting INPs was approximated from the XRD spectra using the Scherer equation as follows: \[ L = \frac{K \cdot \lambda}{\beta_{\text{obs}} \cdot \cos(\theta)} \] (1)

In this equation, \(L\) is particle size (nm), \(\lambda\) is the radiation wavelength (nm), \(K\) is Scherer constant (0.94, usually 0.87 < \(K\) < 1), \(\beta_{\text{obs}}\) is the observed full width at half-maximum intensity (rad), and \(\beta_{\text{instm}}\) is instrumental broadening (rad) as a function of \(2\theta\). The XRD experiments were repeated to check the reproducibility of the results. The repeated experiments showed that the experimental errors were in the range of \(\pm 1 - 1.5\%\) INP diameters.

Transmission electron microscopy (TEM) images were taken from the powder suspensions with a Hitachi H7100 (St George’s, University of London, UK) motorized and digitized stage, high-resolution (0.4 nm) and high-contrast (25 to 125 kV) microscope equipped with a 1024 \(\times\) 1024 pixel digital camera. For the sample preparation, all samples were dropped on carbon foam wafers, and the residual solvent was removed with filter paper.

Specific surface area (SSA) of the samples was measured by N\(_2\) gas adsorption according to the Brunauer–Emmett–Teller (BET) method equipped with a Micromeritics ASAP 2460 surface area and porosity analyzer (Micromeritics Instrument Corp., Norcross, USA). The degassing process was done by heating the samples in vacuum at the temperature of 50 °C and for 48 h. For a better understanding of the preferred adsorption sites in/on the clay platelets for Fe cations before the reduction, the calculated SSA from BET isotherms was compared. Experimental errors were in the range of \(\pm 0.2\%\) SSA.

\[ \text{calculated } \text{SSA} = \sum \text{wt } % \times \text{SSA} \text{ (from BET isotherms)} \] (2)

Cryogenic Mossbauer spectroscopy of the samples was obtained by a constant-acceleration-type Mossbauer spectrometer incorporating either a microprocessor or an Ortec model 6200 multichannel analyzer with 1024 channels operating in the multiscale mode for the data storage. The \(\gamma\)-ray source was \(^{57}\)Co in Pd of 50 mCu (1.85 \(\times\) 109 Bq) nominal strength, and an
argon/methane proportional counter was used as the γ-ray detector.

Oxidation extent and color change of the samples by consuming the ambient oxygen during the time were measured using a colorimeter.

3. RESULTS AND DISCUSSION

Solvent type, iron cation valent, and chemophysics of the MMT layered structures were categorized as parameters affecting the INP particle size and morphology. Cation and clay types as INPs controlling parameters are also studied.

3.1. Solvent Effect. Figure 2 shows the XRD spectra of the INPs produced with various solvents for the dispersing and/or reducing solutions. The average diameters of the ZVINPs approximated from the XRD spectra are presented in Table 2 for the different solvents.

According to Figure 2, adding EtOH and NaOH to the dispersing and reducing agent solutions, respectively, after the solvent for the mixed three is selected, could enhance the probability of Fe oxides and Fe hydroxide production. This could be due to the increasing O2 solubility of more than 5 times compared to that of pure water and the presence of OH groups in the solution.

On the other hand, Table 2 shows that the presence of EtOH and NaOH in water decreased the average particle diameter compared to pure water. According to the results of previous studies, this phenomenon could be due to the hydrogen bonding of EtOH and NaOH with Fe3O4 (magnetite) and FeO (wustite) surfaces during the reduction reaction. These were reported as intermediate states before becoming fully reduced iron to retard the INP growth and its great tendency toward agglomeration because of steric effects coming from van der Waals forces.

3.2. Cation Type Effect. Fe2+ and Fe3+ have different ion diameters and chemical characteristics, and therefore their reduction products are expected to have different interactions with MMT. Figure 3 shows XRD spectra of the ZVINPs produced from different cations.

The resulting particle size was calculated to be 65 and 73 nm for Fe3+ and Fe2+ cations, respectively. As illustrated in the reflection intensities of Figure 3, using Fe2+ decreased Fe2O3 in the solution by increasing FeO as the precursor of Fe3O4 production accelerated. Producing more Fe3O4 made bigger particles. This was in good agreement with the previous findings to illustrate the effect of increasing Fe2+/Fe3+ ratio in producing bigger iron oxides, as suggested by Glavee et al. and Yan and Zhang.

3.3. Clay Host Effect. The TEM images of the Fe3+ nanoparticles produced alone and in the presence of C20A MMT are shown in Figure 4. As shown in Figure 4a, the produced particles tended to form large aggregates, which could adversely affect their scavenging performance.

According to Figure 4b,c, the growth of INPs produced from Fe3+ cation in/on C20A clay platelets and in the selected solvents reduced the average particle diameter from 50 to 10 nm, which is being reported for the first time. The existing OH groups in MMT on the sheets and edges led to more cations being adsorbed as seeds of final INPs and resulted in smaller particles according to the growth kinetics. In addition to the trapping role of chemical groups of the clay surface and edges, the limited interlayer space of MMT could act as a cage for the Fe cations and limited the INP growth during the reduction process. On the other hand, Figure 4b,c shows that the INP growth on and between the clays dispersed the MMT platelets to...
support the oxygen scavenging. Kombaya-Touckia-Linin et al. showed that this INP has a capacity 4 times more than that of an α-tocopherol-based system.68

As illustrated in Figure 4d, removing the selected solvent INPs appeared to agglomerate in MMT edges. As removing the solvent will cause the strong H-bonding of solvent reduction products (INPs and its oxides) to disappear, these products tended to agglomerate by weak van der Waals forces and interacted with OH groups on the MMT surface and edges.

Figure 5 shows a schematic view of the clay surface effect on the Fe cation reduction.

3.4. Particle Localization. The calculated and measured SSA from BET isotherms is presented in Table 3 to show the particle localization in/on the clay platelets for Fe cations before the reduction.

According to Table 3, adding alkylammonium ions to C20 compared to adding to CNa+, despite of increasing the d value, decreased the SSA from 47.00 to 9.33 g/m² by the steric effect of alkyl chains. Alkylammonium tallow occupied the available interlayer sites for N₂ in the same way as for Fe cations. This strong SSA reduction showed that most nitrogen adsorption sites were between the clay layers.

When INP was produced on the CNa⁺ clays, the measured SSA (41.34 g/m²) was lower than the calculated one of individual components (45.31 g/m²). This result suggested that rather than being only juxtaposed to clays, a significant percentage of INPs were located between the clay layers, contributing to the decrease of SSA by occupying nitrogen absorption sites. On the contrary, when INP was produced on the C20A clays, the measured SSA (16.06 g/m²) was slightly higher than the calculated one (13.02 g/m²).

In the case of C20A, the SSA increase from 9.33 to 16.06 g/m² showed that some of Fe cations adsorbed to somewhere other than available surfaces for N₂, like solvent-modified edges and created new adsorption sites. In the modifying process of clays, the intensity of both O−H stretching and H−O−H bending modes strongly decreased and showed that organic modifications decreased the hydrophilic character of the material surface, which could be due to ionic bond of the OH⁻ groups with ammonium ions.69 The presence of solvents in the Fe growth step replaced these groups and resulted in adsorbing more Fe cations on these sites.

Cryogenic Mossbauer spectroscopy of Fe³⁺/Fe²⁺ MMT samples were used to investigate the adsorption preference of each Fe ion on CNa⁺ or C20A. The related spectra of Fe³⁺/Fe²⁺ MMT samples are illustrated in Figure 6.

With reference to Mossbauer spectroscopy results, isomer shift (IS), quadrupole splitting (QS), and reflection width (LW) for Fe³⁺ and Fe²⁺ as the main species in each reflection are summarized in Table 4.

The observation that Fe⁴⁺ was found in the Fe²⁺-exchanged samples was in agreement with the work of ref 70, where it was reported that it was too hard to prepare Fe-exchanged MMT without partial oxidation. The parameters of the Fe⁴⁺ species were similar to those from the hydrated Fe²⁺ ion.71,72 The Fe²⁺ ions would, therefore, be separated from the clay surfaces by water molecules (mainly in interlayer space of dried clays) which were immobilized in the frozen state.

For Fe₀₂⁻⁻CNa⁺, an additional component was observed (Figure 6d). By analogy with the Fe²⁺ results, this additional component probably occurred from a solvated ion.

For Fe³⁺, by changing the clay from C20A to CNa⁺, there was no significant change in Mossbauer parameters. In this respect, there could be two possibilities. The first possibility was that Fe³⁺ may be directly bound to the silicate structure. The second one was that hydroxy Fe³⁺ polymers may be formed, as similar parameters had been reported for the various oxyhydroxides.73 If species were surrounded by other molecules like water in cryogenic states, freezing of the surrounding part would change the Mossbauer spectra. Usually, the unchanged state of the
spectra was evidence of direct connection of species to the main structure or forming a polymer.

Figure 7 shows the changing of the intercalation and exfoliation extent in CNa⁺ and C20A by the INP growth from different cations between platelets. The INP produced from Fe²⁺ cations in C20A and CNa⁺ shifted and damped the (001) spectra was evidence of direct connection of species to the main structure or forming a polymer.

Table 3. Specific Surface Area from N₂ BET Isotherms of Dried Powders (INP/MMT 1:6 w/w)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe03 ZVINP</th>
<th>CNa⁺</th>
<th>Fe03- CNa⁺</th>
<th>C20A</th>
<th>Fe03- C20A</th>
</tr>
</thead>
<tbody>
<tr>
<td>measured SSA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(g/m²)</td>
<td>35.17</td>
<td>47.00</td>
<td>41.34</td>
<td>9.33</td>
<td>16.06</td>
</tr>
<tr>
<td>calculated SSA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(g/m²)</td>
<td>45.31</td>
<td></td>
<td>13.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Mössbauer Parameters of Main Species in Produced Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>component</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>LW (mm/s)</th>
<th>area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe03-C20A</td>
<td>Fe³⁺</td>
<td>0.350</td>
<td>0.753</td>
<td>0.535</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>Fe₂⁺</td>
<td>1.220</td>
<td>2.270</td>
<td>0.530</td>
<td>16</td>
</tr>
<tr>
<td>Fe02-C20A</td>
<td>Fe³⁺</td>
<td>0.332</td>
<td>0.790</td>
<td>0.566</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Fe₂⁺</td>
<td>1.210</td>
<td>2.260</td>
<td>0.490</td>
<td>18</td>
</tr>
<tr>
<td>Fe03-CNa⁺</td>
<td>Fe³⁺</td>
<td>0.343</td>
<td>0.766</td>
<td>0.556</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Fe₂⁺</td>
<td>1.200</td>
<td>2.240</td>
<td>0.520</td>
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</tr>
<tr>
<td>Fe02-CNa⁺</td>
<td>Fe³⁺</td>
<td>0.305</td>
<td>0.820</td>
<td>0.555</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Fe₂⁺</td>
<td>1.221</td>
<td>2.314</td>
<td>0.490</td>
<td>24</td>
</tr>
</tbody>
</table>
reflection, respectively, which could originate from the main position of this species in the interlayer and also the bigger size. This was in good agreement with the result obtained from Mossbauer spectroscopy. Growing INPs with a few nanometers size from picometer-sized cations pushed the layers out and resulted in intercalation–exfoliation.

3.5. Oxygen Access to Hybrid Nanostructure. Table 5 represents the color changing process in samples over time by absorbing the ambient oxygen as a qualitative criterion. The colors were obtained by the coordinates in a uniform color space consisting of lightness variable, $L^*$, and chromaticity indices, $a^*$ and $b^*$. There were some facts which could be concluded from this table. First, the color change in ZVINPs was sharp, whereas it was gradual in INP–clays, which could be due to the retarding effect of the clay. Second, the oxygen absorption was faster and sharper in Fe$^{3+}$-based INP samples than that in Fe$^{2+}$-based ones, showing that most Fe$^{2+}$-based INPs were embedded between the clay platelets and were not available for the oxygen attack. Third, the oxygen absorption in Fe$^{3+}$-based samples was more gradual with a lag time shorter than that of the Fe$^{2+}$-based samples, showing the more surface area in these samples due to the dispersing effect of clay sheets and retarded particle

![Figure 6. Cryogenic Mossbauer spectra: (a) Fe03−C20A, (b) Fe02−C20A, (c) Fe03−CNa+, and (d) Fe02−CNa+. Black dots, experimental data; red dots, misfit = experimental data − fitted data; dark blue line, Fe para; light blue line, Fe magn; green line, solvated ion.](image)

![Figure 7. Changing the extent of intercalation and exfoliation in CNa+ and C20A by INP growth from different cations between clay platelets.](image)
agglomeration. Fourth, CNa\(^+\) clays protected Fe\(^{2+}\) INPs longer and Fe\(^{3+}\) INPs shorter than C20A clays. So the Fe03-CNa\(^+\) hybrid structure could be a choice for fast oxygen scavenging, while Fe02-CNa\(^+\) is the better fit for long lasting scavenging.

Table 5. Color Changing Process in Samples over Time by Absorbing the Ambient Oxygen

<table>
<thead>
<tr>
<th>Time/Sample</th>
<th>Fe03-C20A</th>
<th>Fe02-C20A</th>
<th>Fe03-CNa(^+)</th>
<th>Fe02-CNa(^+)</th>
<th>Fe03 ZVINP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 h</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>1 day</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 days</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3 days</td>
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<td>4 days</td>
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<tr>
<td>6 days</td>
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<td></td>
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<tr>
<td>16 days</td>
<td></td>
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</tbody>
</table>

Figure 8. Localization of different iron nanoparticles on montmorillonite clay hosts for oxygen scavenging: (a) Fe0-MMT with Fe\(^{3+}\) starter and (b) Fe0-MMT with Fe\(^{2+}\) starter.
Based on the information above, localization of different cation-based iron nanoparticles on montmorillonite clays host can be shown as Figure 8. The Fe\textsuperscript{3+} cations tend to embed between clay layers and reduce to Fe\textsuperscript{0} INP (Figure 8a) more easily compared to Fe\textsuperscript{3+} cations, which are solvated and bonded to the surface of clay sheets (Figure 8b). Fe\textsuperscript{0} generation at the clay interlayer could lead to more intercalation.

4. CONCLUSIONS

In this work, size and localization of iron nanoparticles in the presence of natural or modified montmorillonite clays were studied. The results indicated that reducing Fe cations in the presence of montmorillonite, on one hand, limited the particles, and agglomeration resulting in producing dispersed particles, on the other hand, led to the higher clay intercalation—exfoliation. By changing the cation type of iron particles before reduction and growth, the absorption site on the clay, oxygen scavenging properties of the produced particles, and intercalation—exfoliation state were changed since the Fe\textsuperscript{2+} cations preferred to migrate to the interlayer space while Fe\textsuperscript{3+} tended to bond to the clay surface. Meanwhile, the rate of scavenging in Fe\textsuperscript{3+}-based montmorillonite was more due to availability of iron nanoparticles. Due to the embedding of nanoparticles through the interlayer space, Fe\textsuperscript{3+}-based montmorillonite had more shelf life and its migration probability in the polymer was less than that of embedded Fe\textsuperscript{0}.

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Notes

The authors declare no competing financial interest.

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