Selective Synthesis of Manganese/Silicon Complexes in Supercritical Water

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A series of manganese salts (Mn(NO₃)₂, MnCl₂, MnSO₄, and Mn(Ac)₂) and silicon materials (silica sand, silica sol, and tetraethyl orthosilicate) were used to synthesize Mn/Si complexes in supercritical water using a tube reactor. X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) were employed to characterize the structure and morphology of the solid products. It was found that MnO₂, Mn₂O₃, and Mn₂SiO₄ could be obtained in supercritical water at 673 K in 5 minutes. The roles of both anions of manganese salts and silicon species in the formation of manganese silicon complexes were discussed. The inorganic manganese salt with the oxyacid radical could be easily decomposed to produce MnO₂/SiO₂ and Mn₂O₃/SiO₂. It is interesting to found that Mn(Ac)₂ can react with various types of silicon to produce Mn₂SiO₄. The hydroxyl groups of the SiO₂ surface from different silicon sources enhance the reactivity of SiO₂.

1. Introduction

Recently, the growth of manganese silicate (Mn₃SiO₄) and manganese dioxide (MnO₂) barrier layers on the SiO₂ surface through the deposition of metal Mn and Mn/Cu alloys after high temperature annealing has attracted considerable investigations [1, 2]. These self-forming diffusion barrier layers can effectively prevent the diffusion of Cu, O, and H₂O and have been proposed as a scalable alternative to Ta/TaN barrier layers in the future [3, 4]. However, the synthesis method employed was limited to high temperature annealing and the unreacted metallic Mn still remained after the formation of barrier layer, which would diffuse to the surface of the deposited Cu interconnect. Moreover, the uncertainty of chemical composition of products undermined the potential application of this barrier layer [5, 6]. Furthermore, the low-valence manganese oxides, supported and unsupported, have attracted great attentions as catalytically active components in a variety of catalytic reactions, for example, the selective catalytic reduction of NO with NH₃ [7, 8], the oxidation of alcohol [9, 10], and the removal of hydrogen sulfide [11]. Various active manganese oxides and dispersion of particles can be obtained using different precursors and preparation methods, which seriously influence the activity of the catalysts in catalytic reactions or other utilizations.

Supercritical water (SCW, above 647 K and 22.1 MPa) can provide an excellent reaction environment for hydrothermal synthesis. The physical and chemical properties of water, such as viscosity, diffusion coefficient, dielectric constant, and ionic product, vary dramatically around the critical point depending on the state variables (pressure, temperature, and density) [12–14]. These properties make fast reaction rate and crystal nucleation rate which leads to high degree of crystallinity, small grain size, and narrow size distribution of the produce materials [15]. The size and morphology of the produced particles can be controlled by the pressure and temperature during preparation [16]. In addition, there is no liquid-gas interface and surface tension in...
the supercritical state, and a homogenous reducing or oxidizing atmosphere can be obtained by introducing oxygen, hydrogen, or other gases [17, 18]. The supercritical hydrothermal synthesis method can also synthesize many materials that conventional hydrothermal synthesis method or solid-phase synthesis cannot synthesize. Thus, these specific properties of supercritical water have contributed to its widespread applications in materials synthesis [19–22], catalysis [23–25], and semiconductor [26, 27].

Our recent work found that the precursor of Mn plays a crucial role during the supercritical water impregnation, and MnO and Mn2SiO4 can be obtained from Mn(NO3)2 and Mn(AC)2·4H2O reacting with Si species containing in coal-derived active carbon, respectively [28].

In this work, we proposed a supercritical water synthesis method for the production of Mn2SiO4 and SiO2 supported manganese oxide. A series of manganese salts (Mn(NO3)2, MnCl2, MnSO4, and Mn(AC)2) and silicon materials (silica sand, silica sol, and tetraethyl orthosilicate) were used as raw materials. Three kinds of products (MnO2, Mn2O3, and Mn2SiO4) can be selectively produced by choosing different raw materials. The roles of both anions of manganese salts and silicon sources in the formation of the products under supercritical water conditions were discussed primarily.

2. Experimental

2.1. Materials. Manganese nitrate (50% Mn(NO3)2 in water), manganese chloride (MnCl2), manganese sulfate monohydrate (MnSO4·H2O), manganese acetate tetrahydrate (MnC2H3O2·4H2O), and tetraethyl orthosilicate (C2H5O·Si) were obtained from Aladdin Chemistry Co. (Shanghai, China). JN-30 silica sol, N-butanol (C4H9O), hydrofluoric acid, and silica sand were obtained from Fenghuan Chemistry Co. (Tianjin, China). Distilled and deionized (DDI) water was produced in our lab. The purities of all chemicals except manganese nitrate are above 98%.

2.2. Apparatus. The sample synthesis was conducted using a 16.7 mL stainless steel tube reactor. Figure 1 shows the schematic diagram of the tube reactor system. It was heated by a molten salt bath, and the temperature of salt bath was measured by a K-type thermocouple. The molten salt bath is made of 45 wt% KNO3 and 55 wt% NaNO3. It helps to keep the temperature of the reaction system constant and translate heat fast and uniformly. The reactor can be driven to swing up and down by a motor at a speed of 120 cycles-min⁻¹ over a range from 613 K to 773 K with ±1K error in our synthesis experiments. The pressure was calculated according to the temperature and the content of water in the reactor.

2.3. Synthesis

2.3.1. Reaction of Manganese Salt and Silica Sand. Four metal manganese salts (Mn(NO3)2, MnCl2, MnSO4, and Mn(AC)2) were dissolved in water and the salt solutions were prepared with a concentration of 1 M. Each solution was then fed into the reactor followed by an addition of silica sand. The mole ration of Mn:Si was kept to 1:1 The reactor was immersed into the salt bath when the desired reaction temperature was reached. After the reaction, the reactor was rapidly quenched and cooled to room temperature in a water bath. Every reaction was conducted at the temperature of 673 K with a resident time of 5 minutes. The content of water was 6.0 mL and the corresponding pressure was about as 30 MPa. The products were filtered, washed with distilled water, and dried at 343 K for 12 hours. The solid powders were obtained and characterized.

2.3.2. Reaction of Manganese Salt and Silica Sol. Each manganese salt solution with a concentration of 1 M was added dropwise into the silica gel under magnetic stirring for 10 minutes. The temperature, contents of water, resistant time, and other step were the same as those in Section 2.3.1.

2.3.3. Reaction of Manganese Salt and Tetraethyl Orthosilicate. 10.42 g tetraethyl orthosilicate was mixed with 11.12 g n-butanol under magnetic stirring, in which n-butanol was used to facilitate the followed hydrolysis and condensation reaction. Then as catalyst, a mixture of 9 g water and 0.25 g HF was added dropwise into the mixture. After 25 minutes, the aqueous manganese salt solution with a concentration of 1 M was added and then the mixture was fed into the reactor under the same conditions as those in Section 2.3.1.

2.4. Characterization. The structure of each sample was measured by X-ray diffraction (XRD) using a D/Max-2500 V/PC Rigaku X-ray diffractometer (Japan) with a Cu Kα radiation source ($\lambda = 0.1543$ nm) at room temperature in the range of $2\theta = 5–80^\circ$. The system was operated at 100 mA and 40 kV.

The morphology of each sample was studied using a JEOL JSM-7001F scanning electron microscope (SEM).

X-ray photoelectron spectroscopy (XPS) was conducted to determine the surface concentration and binding energy of Mn 2p3/2, using a Kratos AXIS Ultra DLD spectrometer (Shimadzu, Japan) equipped with a monochromated Al
Ka source (hv = 1486.6 eV, 75 W). The spectrometer was calibrated using the photoemission lines of Au (Au 4f/2 = 83.95 eV), Ag (Ag 3d/2 = 368.2 eV), and Cu (Cu 2p3/2 = 932.62 eV). No smoothing routine of data was applied to analyze the results.

The crystalline phases of samples were measured by transmission electron microscopy (TEM) at room temperature with a JEM-2010 microscope operating at 200 kV.

3. Results and Discussion

3.1. XRD Characterization. XRD patterns of the samples synthesized by different manganese salts and silica sand in supercritical water are shown in Figure 2. The diffraction peaks of SiO₂ crystal and MnO₂ crystal can be identified in the XRD patterns of the sample (A1) prepared by Mn(NO₃)₂ and silica sand. Moreover, the intensity of SiO₂ diffraction peak is much higher than that of MnO₂. This means that the crystal form or the degree of crystallinity of SiO₂ is far better than that of MnO₂ in A1. However, all the diffraction peaks of samples (A2 and A3) synthesized by the two kinds of manganese salts (MnCl₂ and MnSO₄) reacted with silica sand clearly show the appearance of SiO₂ only. The characteristic peaks of samples (A4) obtained by the reaction of Mn(Ac)₃ and silica sand indicate Mn₂SiO₄ and SiO₂ crystal although the peak intensity of Mn₂SiO₄ (the inset in Figure 2) is very low. Based on above results, it can be concluded that Mn(NO₃)₂ and Mn(Ac)₃ can react with silica sand in supercritical water at 673 K for 5 minutes and the main products are MnO₂ and Mn₂SiO₄, respectively.

XRD patterns of the samples prepared by different manganese salts and silica sol in supercritical water are given in Figure 3. The diffraction peaks of Mn₃O₄ crystal can be found in the XRD patterns of the samples B1 and B3. This means that both Mn(NO₃)₂ and MnSO₄ can react with silica sol to produce Mn₃O₄ at 673 K for 5 minutes. The broad peak at about 22° can be attributed to the amorphous SiO₂ hydrolyzed by the silica sol. There is no diffraction peak except the characteristic peak of the amorphous SiO₂ in the XRD pattern of the sample B2. It indicates that MnCl₂ cannot react with silica sol and only amorphous SiO₂ can be obtained from this reaction. It is noted that the good crystalline for Mn₂SiO₄ in sample B4 was obtained from the reaction between Mn(Ac)₃ and silica sol. Note that the SiO₂ characteristic peaks in B4 cannot be resolved. The reason may be that they are marked by the peaks of the crystalline Mn₂SiO₄. It can be concluded that Mn(NO₃)₂, MnSO₄, and Mn(Ac)₃ can react with silica sol in supercritical water at 673 K for 5 minutes and the main products are Mn₂O₃ and Mn₂SiO₄.

Figure 4 shows the XRD patterns of samples prepared by different manganese salts and tetraethyl orthosilicate in supercritical water. It is found that the crystalline Mn₂SiO₄ was produced by the reaction of Mn(Ac)₃ and tetraethyl orthosilicate (C₁). Both Mn(NO₃)₂ and MnSO₄ can react with tetraethyl orthosilicate to generate Mn₂O₃ in supercritical water. It should be noted that no characteristic peaks of SiO₂, crystalline or amorphous, can be observed in the XRD pattern of C₁. It also can be found that MnCl₂ could not react with tetraethyl orthosilicate in the cases of silicon sand and silica sol. Tetraethyl orthosilicate can also produce the amorphous SiO₂ in supercritical water.

Based on the XRD analyses, it can be concluded that Mn(Ac)₃ is the best manganese precursor among the four manganese salts to synthesize Mn₂SiO₄ in supercritical water. Both Mn(NO₃)₂ and MnSO₄ can produce Mn₂O₃ or MnO₂.
while MnCl$_2$ could not react with any of the three kinds of silicon materials.

On the aspect of silicon source, tetraethyl orthosilicate and silica sol have similar activity and both can react with Mn(Ac)$_2$ to produce Mn$_2$SiO$_4$. Silica sand has the least reactive among the three kinds of silicon sources and only Mn(Ac)$_2$ can react with it to generate small amount of Mn$_2$SiO$_4$ in supercritical water. That is due to the high stability of the SiO$_2$ crystal which is the main component of silicon sand. The diffraction peaks from SiO$_2$ of B4 and C4 in Figures 3 and 4 may be covered by that of Mn$_2$SiO$_4$.

3.2. XPS Characterization. The chemical states of the surface species of the representative products were investigated using XPS and the results are presented in Figure 5. And the surface atomic concentrations of samples characterized by XPS results are shown in Table 1. The amounts of Mn on the surface of sample A1 are 6.11%, while those of samples B1 and B3 are only 0.70% and 0.39%, respectively. As for the Mn 2p spectra, different products exhibit different binding energies (BE) of Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ levels. The binding energies of the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ in the sample A1 are 642.0 eV and 653.8 eV, which is attributed to MnO$_2$ [28–30]. Similarly, the BE of the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ in the samples B1 and B3 are 641.7 eV and 653.7 eV which can be assigned to MnO$_3$ [28, 29]. This also agrees well with the XRD results. Compared with the Mn 2p spectra of A1, the peak intensities belonging to B1 and B3 are very weak; this is because the surface atomic concentration of samples B1 and B3 is very low. In addition, the BE of the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ in the sample B4 and C4 are in the range of 641.7–642.2 eV and 653.4–653.7 eV, respectively. These may be attributed to Mn$_3$SiO$_4$/MnSiO$_3$, MnO, and/or their mixtures [31]. The peak intensity of B4 is the highest among the five lines, which is in agreement with the surface atomic concentration. The surface atomic concentration of Mn in sample B4 is the highest (7.38%, Table 1).

As for the O 1s region, the BE of O 1s in the sample A1 are 532.5 eV and 529.4 eV, which are attributed to SiO$_2$ and MnO$_2$, respectively [30, 32]. The BE of O 1s in samples B1 and B3 are 532.9 eV, which can be assigned to SiO$_2$ [32]. However, the O 1s peak assigned to MnO$_3$ in samples B1 and B3 is not resolved; it is possibly because the XPS signal of MnO$_3$ in samples B1 and B3 is too weak comparing to SiO$_2$. The BE of O 1s in samples B4 and C4 appearing at the positions of 533.9 eV and 531.6 eV can be attributed to SiO$_2$ and Mn$_3$SiO$_4$/MnSiO$_3$, MnO, and/or their mixtures [31], respectively. As for the Si 2p spectra, the Si 2p peak in sample A1 at 103.2 eV is attributed to SiO$_2$ [32] but is attributed to SiO$_2$ in samples B1 and B3 appearing at the position of 103.7 eV, which shifted slightly higher. The Si 2p peaks in the samples B4 and C4 at 103.5 eV and 102.4 eV are attributed to SiO$_2$ and Mn$_3$SiO$_4$ [31], respectively. Combined with the XRD results, Mn2p XPS spectra, and O1s XPS spectra, the products synthesized by Mn(Ac)$_2$ and silica sol or tetraethyl orthosilicate contain Mn$_2$SiO$_4$ and SiO$_2$.

3.3. TEM Characterization. Figure 6 shows the representative TEM images of all samples. It was revealed that fine particles with high level of dispersion were formed on the bulk products in A1 and the morphology of bulk products was single sphere. Based on the XRD analyses, the fine particles were MnO$_2$, and the bulk products were SiO$_2$. TEM

![Figure 4: XRD patterns of samples prepared by manganese salt and tetraethyl orthosilicate. (C1, C2, C3, and C4 represent the solid products from reaction of Mn(NO$_3$)$_2$, MnCl$_2$, MnSO$_4$, and Mn(AC)$_2$ with tetraethyl orthosilicate, resp.).](image)

![Figure 5: Mn 2p, O 1s, and Si 2p XPS spectra of samples prepared by reaction between different aqueous manganese salt (A1: Mn(NO$_3$)$_2$ with silica sand, B1: Mn(NO$_3$)$_2$ with silica sol, B3: MnSO$_4$ with silica sol, B4: Mn(AC)$_2$ with silica sol, and C4: Mn(AC)$_2$ with tetraethyl orthosilicate, resp.).](image)

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<th>Sample</th>
<th>Mn 2p</th>
<th>O 1s</th>
<th>Si 2p</th>
<th>N 1s</th>
<th>C 1s</th>
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<td>1.06</td>
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<tr>
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<td>29.35</td>
<td>0.35</td>
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<tr>
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<td>27.46</td>
<td>0.26</td>
<td>6.07</td>
</tr>
<tr>
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<td>51.30</td>
<td>15.57</td>
<td>—</td>
<td>25.75</td>
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<tr>
<td>C4</td>
<td>2.99</td>
<td>36.46</td>
<td>4.99</td>
<td>—</td>
<td>55.56</td>
</tr>
</tbody>
</table>

Note: A1, B1, B3, B4, and C4 are the samples from reaction of Mn(NO$_3$)$_2$ with silica sand, Mn(NO$_3$)$_2$ with silica sol, MnSO$_4$ with silica sol, Mn(AC)$_2$ with silica sol, and Mn(AC)$_2$ with tetraethyl orthosilicate, respectively.
images of B1 and B3 samples were similar: highly dispersed fine particles were formed on top of the bulk products, and the bulk products were uniform spheres with a diameter of approximate 20 nm. These spheres were bonded together and formed some irregular rings with a diameter of about 40 nm. Based on the XRD analyses, the fine particles should be Mn$_2$O$_3$, and the bulk products should be SiO$_2$. TEM images of samples B4 and C4 were similar: stick-like products were obtained with a length of about 200 nm. The chemical composition of products may be Mn$_2$SiO$_4$ or a mixture of Mn$_2$SiO$_4$ and SiO$_2$.

3.4. SEM Characterization. SEM micrographs of the solid products were shown in Figure 7. The products obtained by different manganese salts reacting with silica sand are some fine particles and irregular flaky polyhedron. While the products generated by reactions between different salts (Mn(NO$_3$)$_2$, MnSO$_4$, and MnCl$_2$) and silica sol or tetraethyl
orthosilicate are regular spheres and fine particles, the products formed by Mn(Ac)$_2$ and silica sol or tetraethyl orthosilicate are slightly different, agglomerated to be unregular ellipsoid and flaky polyhedron.

3.5. Reaction Mechanism. The main products synthesized from four kinds of manganese salts and three kinds of silicon sources under supercritical water conditions are one or several of the followings: SiO$_4$, MnO$_2$, Mn$_2$O$_3$, and Mn$_3$SiO$_4$. And the reaction mechanism will be discussed in this section.

The SiO$_2$ gel micronucleus can be formed by the hydrolysis and condensation reaction of tetraethyl orthosilicate. This is a fast and environmentally friendly process, and the reaction equation can be expressed as follows:

$$\text{Si(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \xrightarrow{\text{HF}} 4\text{C}_2\text{H}_5\text{OH} + \text{Si(OH)}_4$$

(Hydrolysis)

$$n\text{Si(OH)}_4 \xrightarrow{\text{HF}} n\equiv \text{Si} - \text{OH} + \text{mH}_2\text{O}$$

(Condensation [39])

All the manganese salts can hydrolyze first in the water:

$$\text{MnX}_{2y} \equiv \text{Mn}^{2+} + \frac{2}{y}X^{2-}$$

(Dissociation) (2)

(X is NO$_3^-$, SO$_4^{2-}$, Cl$^-$, and Ac$^-$, and y = 1, 2)

$$\text{Mn}^{2+} + 6\text{H}_2\text{O} \equiv \text{Mn}^{2+}(\text{H}_2\text{O})_6$$

(Hydrolysis) (3)

The reaction equilibrium biases in favor of the left under atmospheric conditions. However, under the supercritical condition, the reaction equilibrium biases in favor of the right [33, 34] and the radical ion under acidic conditions such as NO$_3^-$ will be decomposed. Chistunoff et al. [35, 36] investigated the decomposition of aqueous HNO$_3$ solution in supercritical water and reported that NO$_2$ or HNO$_3$ and O$_2$ can be formed at 673 K. If a reducing agent was added, NO and N$_2$O can be generated. The reaction equation of hydrothermal decomposition and oxidation can [27, 33, 34] be expressed as follows:

$$(5 - 2x)\text{Mn}^{2+}(\text{H}_2\text{O})_6 + 2\text{NO}_3^- \equiv (5 - 2x)\text{MnO}_2 + 2\text{NO}_x$$

$$+ (26 - 10x)\text{H}_2\text{O} + (8 - 4x)\text{H}$$

(Hydrothermal decomposition and oxidation [28, 34, 35])

The Mn(NO$_3$)$_2$ can be transformed to MnO$_2$ or Mn$_2$O$_3$ in supercritical water, but only Mn$_2$O$_3$ can be produced from MnSO$_4$ in supercritical water. This may be attributed to the oxidative capacity of the acid ion in the supercritical water and the effect of hydroxyl ligands generated by the silicon sources. The supercritical water is an oxidative reaction environment due to the dissolved O$_2$ and the NO$_3^-$ has strong oxidative capacity in the supercritical water [37]. Therefore, the Mn$^{2+}$ species in the Mn(NO$_3$)$_2$ supercritical water solution can be oxidized into MnO$_2$, and the SiO$_2$ crystal (silica sand) existing in the supercritical water almost does not affect the reaction. The SO$_4^{2-}$ with weaker oxidative capacity is hard to be decomposed compared with NO$_3^-$ under acidic conditions, so the oxidized Mn species cannot be produced.

The silica sands are crystal particles and the silica sol or tetraethyl orthosilicate has irregular and porous structure. There is almost no hydroxyl groups on the surface of silica sand, but plenty on the surface of the silica hydrolyzed from silica sol or tetraethyl orthosilicate [38]. Hair [39–41] has investigated the hydroxyl groups on silica surface using infrared (IR) gravimetric adsorption at various temperatures. Their results indicated that the maximum water sorption will occur at 673 K where both rehydration of the surface and sorption can occur simultaneously. The hydroxyl groups on the surface of SiO$_2$ can act as ligands. It is easy to combine with Mn$^{2+}$ to form complex which enhances its reactivity. The reaction of MnSO$_4$ with silica sol or tetraethyl orthosilicate can produce Mn$_2$O$_3$, but the Mn(NO$_3$)$_2$ with silica sol or tetraethyl orthosilicate will form Mn$_3$SiO$_4$ while reacting with silica sand and will form MnO$_2$. This may be because the surface hydroxyl ligands suppress the oxidation of Mn$^{2+}$. Cl$^-$ has not oxidative capacity and cannot be decomposed, so there was hardly manganese oxides produced in the supercritical water by reaction of MnCl$_2$ with any silicon sources.

The products prepared by Mn(Ac)$_2$ are obviously different from the other three Mn salts. The reason may be that the Ac$^-$ is a good candidate which is easy to be combined with Mn$^{2+}$ via a ligand exchange reaction to form Mn$^{2+}(\text{H}_2\text{O})_6(\text{Ac}^-)_{6-x}$ instead of the hydrolysis of Mn$^{2+}(\text{H}_2\text{O})_6$ to form Mn oxides according to

$$\text{Mn}^{2+}(\text{H}_2\text{O})_6 + (6 - x)\text{Ac}^- \equiv \text{Mn}^{2+}(\text{H}_2\text{O})_6(\text{Ac}^-)_{6-x}$$

$$+ (6 - x)\text{H}_2\text{O}$$

(Ligands exchange) (5)

The H$_2$O and Ac$^-$ ligands are further exchanged with surface hydroxyl ligands of SiO$_2$, forming Mn$_2$SiO$_4$ and the reaction can be expressed as follows [27, 42]:

$$2\text{Mn}^{2+}(\text{H}_2\text{O})_6(\text{Ac}^-)_{6-x} + \text{HO-Si} \equiv$$

$$\rightarrow \text{Mn}_2\text{SiO}_4 + \text{CO}_2 + \text{H}_2\text{O}$$

(Complexation) (6)

By these ligands exchanging reactions, the Mn$_2$SiO$_4$ loaded on the surface of SiO$_2$ was generated. Due to the different morphology and chemical composition of SiO$_2$, the amount of resulting Mn$_2$SiO$_4$ varied: the silica sol and tetraethyl orthosilicate produced more Mn$_2$SiO$_4$ for more surface hydroxyl ligands and amorphous surface which is easy to interact with the reactants, while the silica sand has fewer hydroxyl ligands and regular crystal structure which leads to poor reactivity.
4. Conclusions

Reactions of various manganese salts (Mn(NO$_3$)$_2$, MnCl$_2$, MnSO$_4$, and Mn(Ac)$_2$) and various silicon sources (silica sand, silica sol, and tetraethyl orthosilicate) have been investigated in supercritical water using a tube reactor. It is found that the anion of manganese salt has a significant effect on the composition of products. The inorganic manganese salt with the oxyacid radical, which is easy to be decomposed, can produce MnO$_2$/SiO$_2$ and Mn$_2$O$_3$/SiO$_2$. The organic manganese salt with ligands like Mn(Ac)$_2$ can react with various types of silicon to generate Mn$_2$SiO$_4$. The hydroxyl groups on the surface of SiO$_2$ from different silicon sources enhance the reactivity of SiO$_2$. Depending on the applications, the selective materials can be fast synthesized in supercritical water by choosing different Mn salt precursor and different types of silicon sources.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


[17] J. W. Kang, “Small capacity decay of lithium iron phosphate (LiFePO$_4$) synthesized continuously in supercritical water:


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