



Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Full Length Article

Location and size regulation of manganese oxides within mesoporous silica for enhanced antibiotic degradation

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ARTICLE INFO

Article history:

Received 13 May 2021

Received in revised form 30 July 2021

Accepted 4 August 2021

Available online 25 August 2021

Keywords:

Advanced oxidation processes (AOPs)

Sulfate radical

Antibiotic degradation

Manganese

Mesoporous silica

ABSTRACT

Refractory antibiotics in domestic wastewater are hard to be completely eliminated by conventional methods, and then lead to severe environmental contamination and adverse effects on public health. In present work, advanced oxidation processes (AOPs) are adopted to remove the antibiotic of sulfachloropyridazine (SCP). Nanosized Mn_2O_3 was fabricated on the SBA-15 material to catalytically activate potassium peroxydisulfate (PDS) to generate reactive oxygen radicals of $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ for SCP degradation. The effects of location and size of Mn_2O_3 were explored through choosing either the as-made or template-free SBA-15 as the precursor of substrate. Great influences from the site and size of Mn_2O_3 on the oxidation activity were discovered. It was found that Mn_2O_3 with a large size at the exterior of SBA-15 (Mn-*t*SBA) was slightly easier to degrade SCP at a low manganese loading of $1.0\text{--}2.0\text{ mmol}\cdot\text{g}^{-1}$; however, complete SCP removal could only be achieved on the catalyst of Mn_2O_3 with a refined size at the interior of SBA-15 (Mn-*as*SBA). Moreover, the $\text{SO}_4\cdot^-$ species were revealed to be the decisive radicals in the SCP degradation processes. Exploring the as-made mesoporous silica as a support provides a new idea for the further development of environmentally friendly catalysts.

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1. Introduction

Organic pollutants in wastewater are harmful to the ecological environment and mankind healthiness, and pose a big challenge to traditional sewage treatment for complete elimination [1–3]. Nowadays, removal of these refractory contaminants has aroused worldwide attention, and several techniques, such as adsorption [4,5], filtration [6,7] and catalysis [8–10], have been employed. Among the options, advanced oxidation processes (AOPs) have demonstrated the competing merit in the complete decomposition [11–13]. During AOPs, highly reactive oxygen species (ROS) such as $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ are produced to decompose toxic organic pollutants into harmless water, carbon dioxide and mineralized acids/salts [14–16]. ROS can be generated from some oxidants, for instance, peroxymonosulfate (PMS) [17–19] and peroxydisulfate (PDS) [20–23], with the assistance of catalysts. Cobalt compounds are

widely used as the catalysts, however, these materials are always confronted with the issue of high content of metal ion leaching, leading to secondary pollution to the water [24,25]. In order to resolve the problem, environmentally friendly manganese based compounds are suggested to be applied [26,27]. For achieving high dispersion and catalytic activity, they are always distributed onto some substrates with large surface areas, such as zeolites [28,29], mesoporous silica [30–32] and carbon materials [33,34].

Mesoporous silica materials (MSM) have attracted much attention since their discovery [35–37]. As one of the most classical and popular MSMs, SBA-15 shows salient features of large surface area, moderate pore diameter and stable mesoporous structure [38,39]. For decades, various metal oxides, for instance, cobalt oxides [40,41], iron oxides [42,43] and copper oxides [44,45], have been loaded on SBA-15. Some researchers also focused on loading manganese oxides on SBA-15. However, the reported Mn_2O_3 nanocrystals were usually of a large average size and present at the outer surface of SBA-15 [46–48]. It could stand to a reason that the dispersion degree of Mn_2O_3 on SBA-15 in previous works was restricted. Up to now, precisely loading nanosized Mn_2O_3 at the

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interior of mesoporous SBA-15 is still a significant challenge. It is well established that the activity of catalysts that are formed by supported metal species is significantly determined by the number of accessible outer surface of these active metal sites [49,50]. Reactant precursors are only able to contact with the accessible outer surface of active metal sites. When it comes to the inner parts, they are usually ineffective, because of the inaccessibility. Thus, it is favorable to regulate the site and size of the metal compounds to expose more accessible surfaces.

Sulfachloropyridazine (SCP) has been extensively used as an antibiotic to prevent or cure bacterial infections in humans and animals on account of its low cost and satisfactory curative effect [51,52]. However, the associated pollution from its unmanaged discharge has become a big issue over the past few years. For instance, in some water samples in China, SCP content shows a concerning high value of $47 \mu\text{g}\cdot\text{L}^{-1}$ [53]. This not only gives rise to negative environmental impact but also leads to enhancing bacterial resistance to human's healthy bodies. Therefore, there is a pressing need to remove SCP from water.

Herein, Mn_2O_3 nanocrystals are fabricated on SBA-15 to activate PDS for SCP degradation. Notably, by using the as-made SBA-15 (*asSBA*) containing P123 to directly incorporate manganese nitrate, the size of Mn_2O_3 nanoparticles in the resulting *Mn-asSBA* is successfully regulated down to smaller than the pore diameter of substrate. Furthermore, the Mn_2O_3 nanoparticles are present at the interior of ordered mesoporous channels of SBA-15 (Scheme 1). In comparison, when P123 is removed prior to the introduction of manganese nitrate to obtain template-free SBA-15 (*tfSBA*), the size of Mn_2O_3 particles in *Mn-tfSBA* is as large as around 20 nm, which remarkably exceeds the pore diameter of the support, suggesting unfavorable dispersion status. It is also demonstrated that the 3.0*Mn-asSBA* material in this work displays the best catalytic activity in SCP degradation. 3.0*Mn-asSBA* is the optimal catalyst when compared to not only other *Mn-asSBA* homologues, but *Mn-tfSBA* counterparts. Mechanistic study further shows that $\text{SO}_4^{\cdot-}$ was the major reactive radical in the process of SCP degrada-

tion. This study may provide a new concept on synthesis of efficient AOP catalysts with precise metal sites' control.

2. Experimental

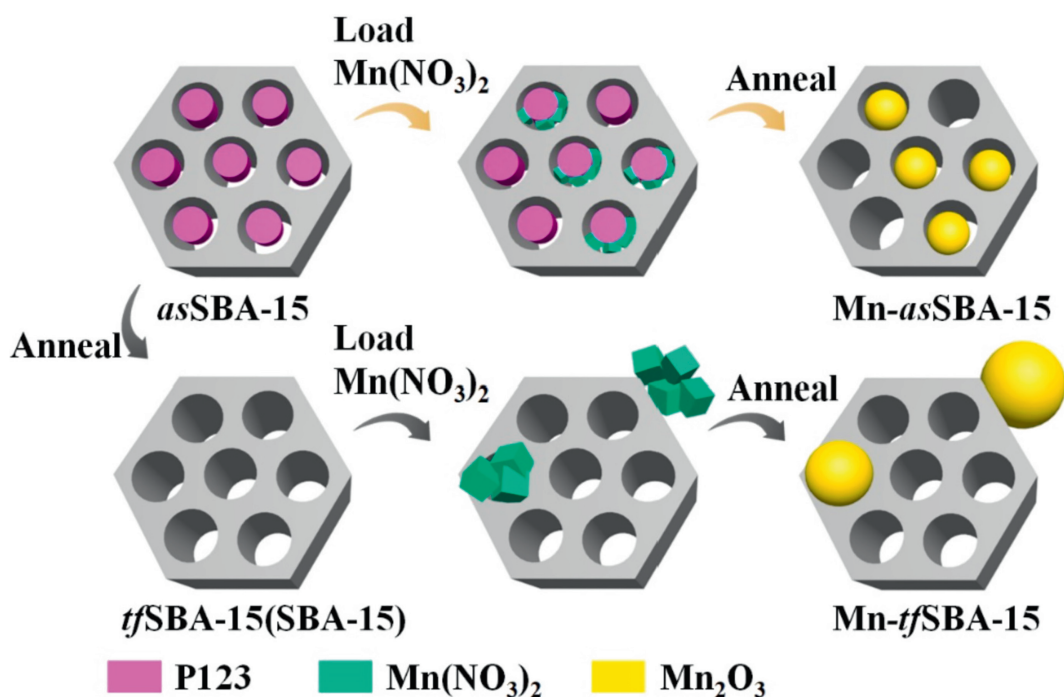
2.1. Preparation of SBA-15, *Mn-asSBA* and *Mn-tfSBA* materials

asSBA-15. The synthesis approach of SBA-15 was based on a classical hydrothermal method [54]. 2 g of P123 was added into 75 g of HCl ($1.6 \text{ mol}\cdot\text{L}^{-1}$) and the suspension was stirred at room temperature until P123 was totally dissolved. Then, the flask was transferred into a constant water bath controlled at 40°C . Afterwards, 4.25 g of TEOS was added into the mixed solution and continuously stirred for 24 h. Subsequently, the overall suspension was transferred into an autoclave, placed into an oven and heated at 100°C for another 24 h. After heating was completed, the suspension in the autoclave was cooled down to room temperature, and the solid products were further filtered and washed with deionized water. Finally, the filter cake was dried and recovered, and the as-made SBA-15 (*asSBA-15*) was obtained.

tfSBA-15 (SBA-15). The *asSBA-15* sample was annealed at 550°C ($2^\circ\text{C}\cdot\text{min}^{-1}$) for 5 h in the air atmosphere to eliminate the P123 template to obtain template-free SBA-15 (*tfSBA-15*), which was also normally called SBA-15.

Mn-asSBA. $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ was loaded on *asSBA-15* through a solid-state grinding process in an agate mortar under atmospheric condition. The grinding was continued for 30 min in order to thoroughly mix the guest and host. Afterwards, the mixed powder was heated in the air atmosphere at 500°C ($2^\circ\text{C}\cdot\text{min}^{-1}$) for 5 h. The resulting catalysts were labelled as *mMn-asSBA*, and the loading amount was *m* mmol of manganese per gram of SBA-15.

Mn-tfSBA. The synthetic procedure was identical to those of *Mn-asSBA-15*, except for using *tfSBA-15* rather than *asSBA-15*. The resultant catalysts were marked as *nMn-tfSBA*, and the loading content was *n* mmol of manganese per gram of SBA-15.



Scheme 1. Fabrication of Mn_2O_3 nanoparticles at the interior of mesopores with a refined size using the as-made SBA-15 (orange route), and at exterior with a large size employing the template-free SBA-15 (black route).

2.2. Characterizations

X-ray diffraction (XRD) was conducted by the instrument of Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation. Low-angle patterns in the 2θ range from 0.7° to 6° were obtained to investigate the structures, and wide-angle patterns from 5° to 80° were acquired to identify the crystal phases. The microstructures were observed using a transmission electron microscope of JEM-200CX. After degassing the samples at 150°C for 4 h, N_2 adsorption–desorption isotherms were obtained at -196°C on a Micrometrics Tristar II Plus to investigate the specific surface areas, pore volumes and pore size distributions. UV–vis profiles were obtained on Agilent Cary 300.

2.3. Catalytic oxidation

The catalytic performances were evaluated by PDS activation to degrade SCP in aqueous solutions. 30 min of adsorption was carried out prior to the catalytic oxidation. The experiment was performed in a batch reactor, and the conditions were as follows: $T = 25^\circ\text{C}$, $[\text{SCP}]_0 = 20\text{ mg}\cdot\text{L}^{-1}$, $[\text{Catalyst}]_0 = 0.2\text{ g}\cdot\text{L}^{-1}$, and $[\text{PDS}]_0 = 2.0\text{ g}\cdot\text{L}^{-1}$. At certain time intervals, 1.0 ml of reaction solution was extracted with a syringe. The solution was further filtered by a $0.22\text{ }\mu\text{m}$ Millipore film, and poured into the HPLC vial. 0.5 ml of methanol was also added to quench the catalytic reaction after the sampling. Then, the SCP concentration was measured by the Shimadzu Nexera X2 3000 UHPLC. A C-18 column was used and the column temperature was set at 30°C . The acetic solution ($\text{pH} = 3.5$) and methanol were chosen as the mobile phases and set at the flow rate of 0.42 and $0.08\text{ ml}\cdot\text{min}^{-1}$, respectively. The concentration of leached manganese after catalysis was evaluated by an inductively coupled plasma optical emission spectrometer (ICP-OES) from PerkinElmer. The removal efficiencies of total organic carbon (TOC) were tested on TOC-V CPH (Shimadzu, Japan). In order to investigate the reactive radical species, the quenching agents of ethanol (EtOH) or *tert*-butyl alcohol (TBA) were added into the initial SCP solution to carry out the catalytic oxidation, with other experimental conditions being identical to those of aforementioned. The electron paramagnetic resonance (EPR) tests were also conducted using a Bruker EMS-plus device to detect the reactive radicals produced during PDS activation, and DMPO ($0.08\text{ mol}\cdot\text{L}^{-1}$) was adopted to trap radicals of $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$.

3. Results and Discussion

The XRD profiles of SBA-15, Mn-asSBA and Mn-tfSBA are shown in Fig. 1. The low-angle XRD patterns (Fig. 1(a) and (c)) show that both Mn-asSBA and Mn-tfSBA possess the identical peaks to that of SBA-15, e.g., distinct (1 0 0), (1 1 0) and (2 0 0) peaks, which are the feature of good ordering of hexagonal $p6mm$ structures [55]. This indicates that the two-dimensional mesoporous structure of the original SBA-15 support is well maintained after the loading of the manganese species. It is further found that the intensities of these featured reflections decrease along with the increase of the manganese content. This may result from the guest loading, which declines the scattering difference between pore spaces and walls. The loading amount of manganese per gram of SBA-15 was adjusted by changing the amount of manganese precursors and further quantified by ICP-OES (Table 1).

Fig. 1(b) and (d) displays the wide-angle XRD results. All the samples display a broad peak at 2θ of 23° , which can be assigned to amorphous silica [56]. On the profiles of 1.0–2.0Mn-asSBA, there are no new diffraction peaks. The undetectable manganese might be because of the low concentration as well as good dispersion.

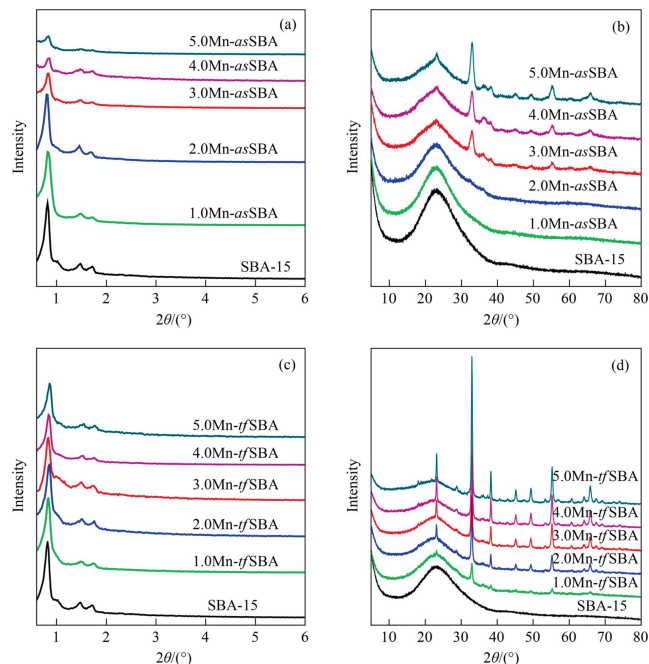


Fig. 1. (a, c) Low-angle and (b, d) wide-angle XRD profiles of SBA-15, Mn-asSBA and Mn-tfSBA samples.

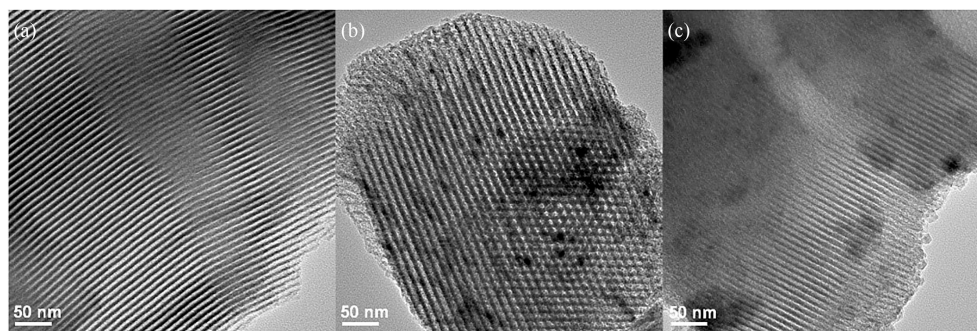
As for other Mn-asSBA samples with loading amount from 3.0 to 5.0, some diffraction peaks at 2θ of 23.1° , 32.9° , 38.2° , 45.2° , 49.3° , 55.2° and 65.8° emerge, which can be vested in the (2 1 1), (2 2 2), (4 0 0), (3 3 2), (4 3 1), (4 4 0), and (6 2 2) planes of Mn_2O_3 , respectively (JCPDS No. 41-1442). The average particle size of Mn_2O_3 is $7.1\text{--}8.5\text{ nm}$, as calculated by Scherrer formula on the basis of the main peak at 2θ of 32.9° (Table 1). The counterpart Mn-tfSBA samples exhibit Mn_2O_3 peaks as well, however, the intensities of these peaks are dramatically strengthened in comparison with those of Mn-asSBA. Corresponding average size of Mn_2O_3 particles in Mn-tfSBA is calculated to be around 20 nm .

Morphological information of SBA-15, Mn-asSBA and Mn-tfSBA samples is revealed by the TEM images. As depicted in Fig. 2, the SBA-15 substrate displays regular black and white stripes, suggesting an ordered mesoporous structure. Also, manganese modified samples show distinct mesopores, suggesting the integrity of the SBA-15 substrate. Furthermore, on the image of 3.0Mn-asSBA, some particles with the similar size as the mesopore are visible, which are probable the guest manganese species. This series of particles are obscure on 1.0 and 2.0Mn-asSBA, and substantial on 4.0–5.0Mn-asSBA (Fig. S1) with a uniform size. With regard to 3.0Mn-tfSBA and other Mn-tfSBA samples (Fig. S2), particles are discovered as well. However, their size is found to be irregular and larger than the mesopore as well as those on Mn-asSBA. This is in good accordance with the aforementioned XRD results.

Fig. 3 exhibits the N_2 adsorption–desorption isotherms and pore size distributions of SBA-15, Mn-asSBA and Mn-tfSBA. The isotherm of SBA-15 shows a standard type-IV behavior with a distinct H1 hysteresis loop, suggesting the cylindrical mesopores [57]. Calculations reveal that the BET surface area is $711\text{ m}^2\cdot\text{g}^{-1}$, and pore volume is $0.957\text{ cm}^3\cdot\text{g}^{-1}$ for SBA-15, respectively (Table 1). Besides, the peaks of pore diameters are concentrated at 8.3 and 6.5 nm for adsorption and desorption branches, respectively. The similar types of sorption isotherms with SBA-15 but delayed hysteresis loops are observed on Mn-asSBA, providing the proof of good maintenance of substrate and successful incorporation of guest species. As a result, the Mn-asSBA samples possess smaller BET surface areas ($679\text{--}485\text{ m}^2\cdot\text{g}^{-1}$) and pore volumes (0.954--

Table 1Textural properties of SBA-15, Mn-*as*SBA and Mn-*tf*SBA samples

Sample	Mn loading amount/mmol·(g SBA-15) ⁻¹	$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	$V_p/\text{cm}^3\cdot\text{g}^{-1}$	D_p/nm		$D_{\text{Mn}_2\text{O}_3}^{\text{①}}/\text{nm}$
				Adsorption	Desorption	
SBA-15	—	711	0.957	8.3	6.5	—
1.0Mn- <i>as</i> SBA	1.03	679	0.954	8.2	6.6	—
2.0Mn- <i>as</i> SBA	2.02	645	0.941	8.3	6.6	—
3.0Mn- <i>as</i> SBA	3.03	642	0.845	8.3	6.6	7.1
4.0Mn- <i>as</i> SBA	4.01	495	0.666	8.1	6.5	8.1
5.0Mn- <i>as</i> SBA	5.00	485	0.632	8.1	6.4	8.5
1.0Mn- <i>tf</i> SBA	1.02	547	0.696	7.9	6.3	19.1
2.0Mn- <i>tf</i> SBA	2.03	525	0.672	7.6	6.3	23.3
3.0Mn- <i>tf</i> SBA	3.04	504	0.639	7.6	6.3	23.7
4.0Mn- <i>tf</i> SBA	4.02	432	0.565	7.8	6.3	24.0
5.0Mn- <i>tf</i> SBA	5.02	407	0.549	7.6	6.1, 4.5	25.3

^① Average particle size of Mn_2O_3 calculated by the Scherrer formula.**Fig. 2.** TEM images of the (a) SBA-15, (b) 3.0Mn-*as*SBA and (c) 3.0Mn-*tf*SBA samples.

$0.632 \text{ cm}^3\cdot\text{g}^{-1}$) than SBA-15. In terms of the pore diameters, there is no obvious distinction between Mn-*as*SBA samples and the pure substrate, implying non-existence of pore blockage. The counterpart Mn-*tf*SBA samples show type IV isotherms but with serious delayed hysteresis loops. Further investigation reveals that both the BET surface areas ($547\text{--}407 \text{ m}^2\cdot\text{g}^{-1}$) and pore volumes ($0.696\text{--}0.549 \text{ m}^3\cdot\text{g}^{-1}$) are inferior to not only SBA-15, but also Mn-*as*SBA containing identical manganese amount. What's more, the pore diameters slightly decline to lower than 7.9 and 6.3 nm for adsorption and desorption branches, respectively. Even the pores of 4.5 nm hold the dominant position on the pore size distribution of 5.0Mn-*tf*SBA, therefore, it is inferred that the mesopores of the substrate may be blocked to some extent by part of the guest manganese species.

Fig. 4 displays the UV-vis spectra of Mn-*as*SBA and Mn-*tf*SBA samples. Mn-*as*SBA samples show main absorption bands in the range of 250–400 nm. While absorption bands in 250–600 nm appear on the spectra of the Mn-*tf*SBA analogues. The Mn_2O_3 bulk crystal is reported to show absorption band around 600–1200 nm [58]. Loading Mn_2O_3 on some substrates is probably to lead to the change of the coordination environment of manganese. In addition, the better dispersion of metal oxides is inclined to cause the shorter wavelength of absorption due to the higher energy for $\text{O}^{2-}\text{--Mn}^{3+}$ charge transfer. Therefore, the guest Mn_2O_3 in Mn-*as*SBA is deduced to be present with a better dispersion degree than that in Mn-*tf*SBA. This is in good consistence with the aforementioned results of smaller Mn_2O_3 particle size in Mn-*as*SBA than in Mn-*tf*SBA from XRD and TEM results.

Taking the above investigations together, it is rational to arrive at two conclusions. Firstly, both Mn-*as*SBA and Mn-*tf*SBA samples retain the mesoporous structure of SBA-15 substrate. A group of characteristic peaks of hexagonal $p6mm$ symmetry on low-angle XRD patterns, the distinct channels on TEM images and IV-typed

N_2 sorption isotherms collectively illustrate no damage to SBA-15 structure. Secondly, by use of *as*SBA to confine guest manganese, the resultant Mn_2O_3 nanoparticles in Mn-*as*SBA can be adjusted within the mesopores, rather than outside of SBA-15 in Mn-*tf*SBA, so as to achieve the uniform and small size of Mn_2O_3 . No Mn_2O_3 peaks are observable on wide-angle XRD profiles of 1.0 and 2.0Mn-*as*SBA, which is indicative of no particle aggregation. The characteristic Mn_2O_3 diffractions are visible on 3.0–5.0Mn-*as*SBA XRD patterns, and the corresponding average particle size of Mn_2O_3 (7.1–8.5 nm) is close to the pore diameter of SBA-15 support (8.3 nm). From the TEM image, it can be seen that Mn_2O_3 particles show the similar size as the channels and are uniformly dispersed at the interior spaces of mesopores. It is a natural tendency for metal species to aggregate and form big crystals. The small particle size of Mn_2O_3 in Mn-*as*SBA is probably determined by their location, that is to say, being inside the mesopores of SBA-15 can prevent the particles from growing into big crystals. Abundant Si-OH groups (Fig. S3–5) and the extra confined space (Figs. S6–8) in *as*SBA should be the possible reasons for the favorable site and size of Mn_2O_3 in Mn-*as*SBA (supporting information), and the similar conclusion was reported on the catalysts of palladium and nickel modified SBA-15 [59,60]. With regard to the counterpart Mn-*tf*SBA samples, the notably intense Mn_2O_3 XRD diffractions and derived large average particle size of around 20 nm, along with the irregular size of big dots on TEM images, suggesting that the major location of Mn_2O_3 is at the exterior of SBA-15. The shorter wavelength of UV-vis absorption also evidences the better dispersion of Mn_2O_3 in Mn-*as*SBA than that in Mn-*tf*SBA.

The catalytic activity of the prepared manganese based catalysts was estimated by the PDS activation to decompose the refractory antibiotic of sulfachloropyridazine (SCP) in water. Considering that adsorption may proceed along with the catalytic oxidation,

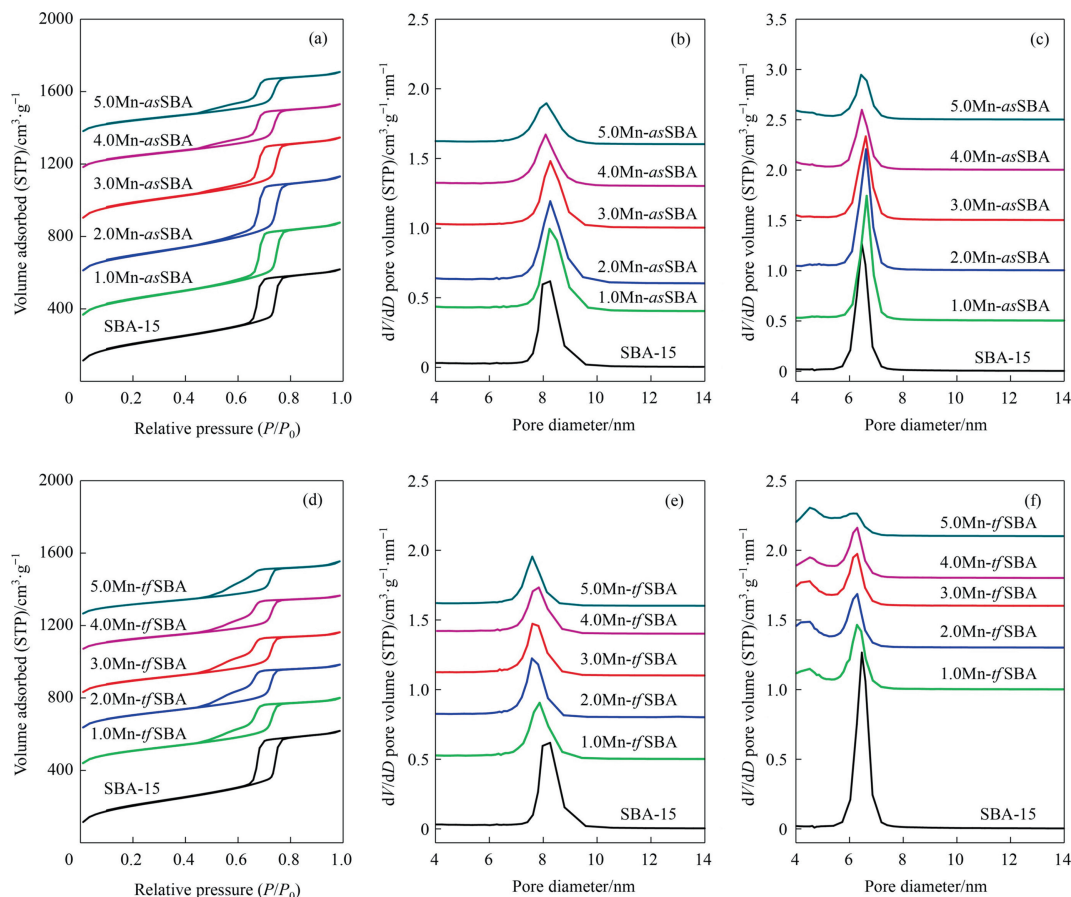


Fig. 3. (a, d) N_2 sorption isotherms, corresponding (b, e) adsorption and (c, f) desorption based pore size distributions of SBA-15, Mn-asSBA and Mn-tfSBA samples. Curves are moved upward for separating with each other.

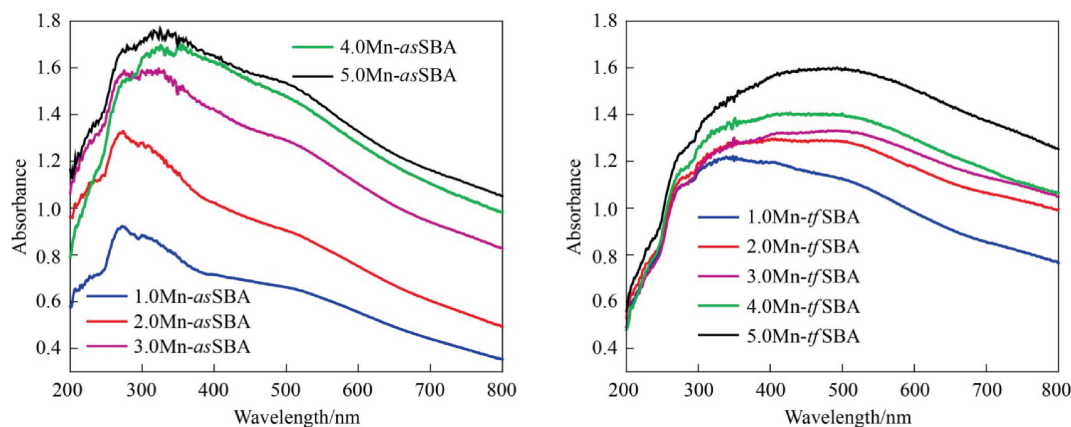


Fig. 4. The UV-vis spectra of Mn-asSBA and Mn-tfSBA samples.

30 min of adsorption was conducted prior to catalysis. As shown in Fig. 5, all the samples can only remove less than 10% of SCP after 30 min of adsorption. In comparison, with self-oxidation, PDS alone eliminated 13.5% of SCP after 360 min, indicating its poor capability for degradation without activation. The SBA-15/PDS system degraded 21.9% of SCP in 360 min, which is slightly better than pure PDS, suggesting the trace effect of SBA-15 on PDS activation. As for the manganese based catalysts of Mn-asSBA and Mn-tfSBA, distinguishable SCP removal was observed with PDS in the solutions. 1.0 and 2.0Mn-asSBA samples attained 56.2% and 69.4% SCP oxidation, respectively. 3.0Mn-asSBA achieved 100% SCP

degradation within 330 min. 4.0 and 5.0Mn-asSBA manifested declined performances of 93.9% and 82.8% SCP removal. It was therefore found that 3.0Mn-asSBA demonstrated the best performance. Then, excessively increasing the manganese amount led to inferior efficiencies. After 360 min of reaction, manganese ion leaching was also investigated, and a negligible value of $0.62 \text{ mg} \cdot \text{L}^{-1}$ (2.3%) was detected for the optimal 3.0Mn-asSBA catalyst.

The 1.0–5.0Mn-tfSBA analogues provided 75.0%, 85.3%, 87.1%, 86.0% and 60.0% of SCP degradation in 360 min in pace with the manganese content from 1.0 to 5.0 mmol·g⁻¹. Unexpectedly, 1.0

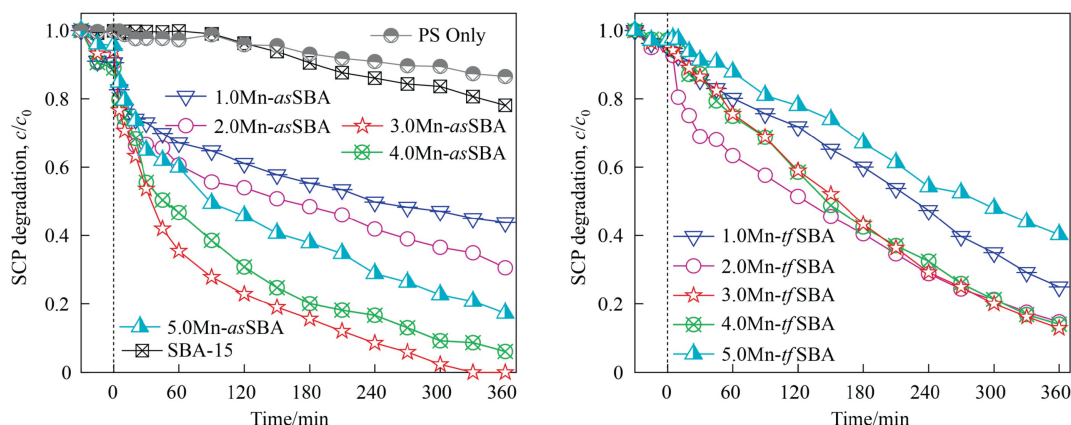


Fig. 5. SCP adsorption and oxidation by PDS activation on SBA-15, Mn-asSBA and Mn-tfSBA. $T = 25\text{ }^{\circ}\text{C}$, $[\text{SCP}]_0 = 20\text{ mg}\cdot\text{L}^{-1}$, $[\text{Catalyst}]_0 = 0.2\text{ g}\cdot\text{L}^{-1}$, and $[\text{PDS}]_0 = 2.0\text{ g}\cdot\text{L}^{-1}$.

and 2.0Mn-tfSBA samples were superior to 1.0 and 2.0Mn-asSBA, respectively. Other Mn-tfSBA samples were inferior to Mn-asSBA with an identical manganese amount, and no Mn-tfSBA reached 100% SCP removal like 3.0Mn-asSBA. It is then plausible to make some conclusions that (i) the manganese species are the active sites in catalysts to activate PDS and drive oxidation; (ii) in combination with aforementioned structural properties, the performance of the active Mn_2O_3 is determined by its site and particle size. To be specific, when the manganese content is at 1.0 and 2.0 $\text{mmol}\cdot\text{g}^{-1}$, Mn-tfSBA can degrade more SCP than Mn-asSBA in 360 min. In this case, Mn_2O_3 is outside of SBA-15. That is to say, at a low manganese loading content, Mn_2O_3 at the exterior of SBA-15 is favorable for the catalytic oxidation. Otherwise, 3.0–5.0Mn-asSBA samples are superior to 3.0–5.0Mn-tfSBA samples with identical manganese content, respectively. In this circumstance, the size of Mn_2O_3 particles is the determining factor, and a smaller size has a positive effect on degradation. Overall, in this work 3.0Mn-asSBA is the optimal catalyst that is able to realize 100% antibiotic elimination. Since the TOC removal was imperative in the process of water treatment, we investigated the removal efficiencies of TOC after 360 min of reactions. The results revealed that 22.3% of TOC was removed on 3.0Mn-asSBA, while only 17.8% on 3.0Mn-tfSBA.

In order to investigate the reactive oxygen species (ROS) from PDS activation to degrade SCP, EPR tests with DMPO as the radical trapping agent were conducted. As profiled in Fig. 6(a), no regular signals are detected on either 3.0Mn-asSBA/DMPO or PDS/DMPO system, revealing that neither 3.0Mn-asSBA nor PDS alone is able to induce PDS activation and radical generation. Notably, charac-

teristic peaks of both $\text{DMPO}\cdot\text{OH}$ and $\text{DMPO}\cdot\text{SO}_4^{\cdot-}$ adducts are observable on 3.0Mn-asSBA/PDS/DMPO system, indicating the generation of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals during AOPs. To further probe the key radicals during SCP degradation, classical quenching experiments were performed. Ethanol (EtOH) was widely employed as a scavenger for both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$, and *tert*-butyl alcohol (TBA) was reported to be capable of quenching $\cdot\text{OH}$ rather than $\text{SO}_4^{\cdot-}$ [42]. Based on this, EtOH and TBA were added into the reaction solutions respectively for the purpose of probing the changes of the reaction rates. As can be seen in Fig. 6(b), the addition of TBA (0.2 $\text{mol}\cdot\text{L}^{-1}$) slightly declined the SCP oxidation from 100% in 330 min down to 92.7% in 360 min. However, the addition of EtOH gave rise to only 78.8% SCP degradation in 360 min. To gain more insight, the reaction rate constant (k) on the basis of a pseudo-first-order was calculated to be 0.017 min^{-1} for the original solution, 0.016 min^{-1} for adding TBA, and 0.004 min^{-1} for adding EtOH, respectively. The feeble influence of TBA and dramatic impact of EtOH elucidated that $\text{SO}_4^{\cdot-}$ radicals were the dominant ROS for SCP degradation on 3.0Mn-asSBA/PDS system. To this end, the path for SCP oxidation can be proposed as follows:

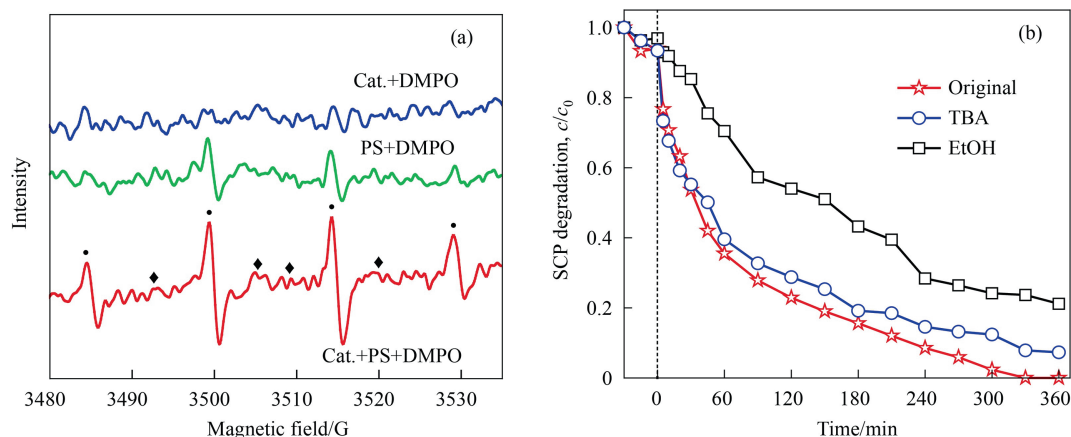
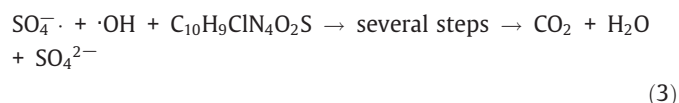


Fig. 6. (a) EPR spectra at 1 min and (b) influence of quenching agents on SCP degradation for the 3.0Mn-asSBA sample. ($T = 25\text{ }^{\circ}\text{C}$, $[\text{SCP}]_0 = 20\text{ mg}\cdot\text{L}^{-1}$, $[\text{Catalyst}]_0 = 0.2\text{ g}\cdot\text{L}^{-1}$, and $[\text{PDS}]_0 = 2.0\text{ g}\cdot\text{L}^{-1}$, $\text{DMPO}\cdot\text{OH}$: $\bullet$, $\text{DMPO}\cdot\text{SO}_4^{\cdot-}$: $\blacklozenge$).

4. Conclusions

In summary, Mn_2O_3 was fabricated on mesoporous silica support to synthesize AOP catalysts for antibiotic removal. Precise control of the location and particle size was achieved by feasibly employing either as-made SBA-15 or template-free SBA-15 in the catalysis synthesis. The as-made SBA-15 facilitated the resultant Mn_2O_3 at the interior of SBA-15 with a small size (Mn-asSBA), while, template-free SBA-15 resulted in irregular and large Mn_2O_3 particles at the exterior of SBA-15 (Mn-*tf*SBA). When the loading content of manganese was as low as $1.0\text{--}2.0\text{ mmol}\cdot\text{g}^{-1}$, Mn-*tf*SBA showed a better AOP efficiency than Mn-asSBA. Once increasing the manganese amount up to $3.0\text{--}5.0\text{ mmol}\cdot\text{g}^{-1}$, Mn-asSBA was superior to Mn-*tf*SBA. It was noteworthy that up to 100% removal of SCP was achieved only on the optimal 3.0Mn-asSBA in this work. The good activity for organic degradation was closely related to the successful encapsulation of Mn_2O_3 inside SBA-15 with a small size. It was also demonstrated that $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ radicals were responsible for the oxidation of SCP, and $\text{SO}_4\cdot^-$ played the predominant role. The concept of regulation of the site and particle size should pave the way for developing AOP catalysts with enhanced activity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We would like to show our great appreciation for funding support from National Natural Science Foundation of China (51602133) and State Key Laboratory of Materials-Oriented Chemical Engineering (KL19-05). The authors also express thanks for taking TEM images from the Centre for Microscopy, Characterization and Analysis (CMCA) of the University of Western Australia.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.08.009>.

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