Enhanced Fenton-like degradation of pharmaceuticals over framework copper species in copper-doped mesoporous silica microspheres

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HIGHLIGHTS

- 0.91 wt% Cu could exist in the framework of Cu-MSMs by the binding of Si—O—Cu.
- PHT, IBU and DP disappeared within 75, 120 and 90 min, respectively, in the M_2/H_2O_2 system at neutral pH.
- The leaching of Cu was much lower than the EU directives in the M_2/H_2O_2 system.
- The phenolic products complexed with the framework Cu(II), forming $\equiv Cu$ -ligands.
- $\equiv Cu$ -ligands interacted with H_2O_2 , accelerating the Cu(II)/Cu(I) cycles.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 6 February 2015

Received in revised form 27 March 2015

Accepted 30 March 2015

Available online 4 April 2015

Keywords:

Fenton-like

Framework copper

Mesoporous silica

Pharmaceuticals

Cu-ligands

ABSTRACT

Copper-doped mesoporous silica microspheres (Cu-MSMs) with the coexistence of Cu(I) and Cu(II) were prepared using a hydrothermal process and characterized by several methods. The characterization studies suggested that 0.91 wt% of the copper species could exist in the framework of the mesoporous silica microspheres by chemical binding of Si—O—Cu; excess copper species were located in the extraframework sites, leading to more oxygen vacancies on the surface of the catalysts. The framework Cu of Cu-MSMs was found to be highly effective and stable for the degradation of pharmaceutical pollutants, as demonstrated with phenytoin, ibuprofen and diphenhydramine in the presence of H_2O_2 at neutral pH values. The conversion of the three pharmaceuticals could reach 100% within 75, 120 and 90 min, respectively; the leaching of Cu was much lower than the EU directives and USA regulations. By the studies of electron spin resonance, gas chromatography–mass spectrometry, Fourier-transform infrared spectra, *in situ* Raman spectra and X-ray photoelectron spectroscopy, an interaction process among the framework Cu of Cu-MSMs, pharmaceuticals and H_2O_2 was proposed: During the Fenton-like reaction, the framework $\equiv Cu(I)$ in Cu-MSMs primarily converted H_2O_2 into $\cdot OH$, and $\equiv Cu(I)$ was oxidized to $\equiv Cu(II)$ by H_2O_2 . The pharmaceuticals were attacked by $\cdot OH$ to form phenolic intermediates, adsorbing on the surface of Cu-MSMs, complexing with the framework $\equiv Cu(II)$, forming $\equiv Cu$ -ligands. $\equiv Cu$ -ligands interacted with H_2O_2 and enhanced the reduction rate of $\equiv Cu(II)$, resulting in the more $\equiv Cu(I)$ production; consequently, accelerated the Cu(II)/Cu(I) cycles on the catalyst surface, leading to more $\cdot OH$ generation for the pharmaceuticals oxidation.

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1. Introduction

Pollution from pharmaceutical compounds (PhACs) in surface and ground waters is an environmental concern in many countries [1,2]. Although the detected concentration levels of PhACs in

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aqueous environment are low and often range from ng/L to $\mu\text{g/L}$ levels, the potential dangers to human and ecological health exist due to long-term exposure [3]. PhACs show a wide range of persistence in aquatic environments, and most of them are highly persistent, which could not be completely eliminated by the conventional water treatment [4].

Among the advanced oxidation processes (AOPs), the Fenton process is a powerful method to produce the high oxidation potential of the hydroxyl radical ($\cdot\text{OH}$) for the degradation of the recalcitrant organic pollutants [5,6]. However, the application of the classic Fenton process (dissolved Fe^{2+} and H_2O_2) is limited by the narrow working pH range of 2–3 as well as the separation and recovery of the iron species [7]. In order to address these problems, heterogeneous Fenton catalysts such as montmorillonites [8], zeolites [9], and metal oxides [10] were developed for use instead of the homogeneous Fenton process. These developed heterogeneous catalysts avoid the need for large amounts of reducing metal ions, which has been an active research area in this field. However, most of them showed good catalytic activity from pH 3 to 5, and a few of them showed significant catalytic efficiency at neutral pH values in water. It has been accepted that H_2O_2 is decomposed into $\cdot\text{OH}$ by the cycle of reduction state (M^{n+}) and oxidation state ($\text{M}^{(n+m)+}$) of the metal with the reduction of $\text{M}^{(n+m)+}$ to M^{n+} by oxidizing H_2O_2 being the rate-limiting step in the overall reaction [11,12]. For example, Fe(III)/Fe(II) cycling is heavily retarded by the slow step of H_2O_2 reducing Fe(III) due to the low rate constants ($0.001\text{--}0.02\text{ M}^{-1}\text{ s}^{-1}$) in neutral condition [12], which often need the aid of ultrasound and UV/visible light irradiation, increasing the energy requirements and the cost for water treatment.

Recently, Cu-based catalysts have attracted considerable attention because the redox properties of copper are similar to iron, and the Cu-based Fenton-like system could work over a broader pH range than the Fe-based redox system [13,14]. Importantly, the reduction of Cu(II) by H_2O_2 ($4.6 \times 10^2\text{ M}^{-1}\text{ s}^{-1}$) occurs more easily than that of Fe(III), and the Cu(I)– H_2O_2 system, which possesses a higher reaction rate ($1 \times 10^4\text{ M}^{-1}\text{ s}^{-1}$) than the Fe(II)– H_2O_2 system ($76\text{ M}^{-1}\text{ s}^{-1}$), can efficiently produce $\cdot\text{OH}$ [13,15,16]. Due to the mobilization of Cu(II)/Cu(I) in water, copper has been suggested to be supported on a porous solid substrate. Cu/13X [17], Cu/SBA-15 [18], and Cu-containing MFI [19] zeolites have been reported as catalysts for wet peroxide oxidation of different organic pollutants. But up to now, the correlation between the copper state in the structure of the catalysts and their catalytic activity was still unclear. Moreover, Cu(II) is easily complexed with organic substances [20], which may be used to enhance the catalytic activity [21]. However, the complexing of organic ligands with metal could accelerate the release of metal ions in aqueous solution from the solid catalyst, destructing the structure of the catalyst [22]. It was found that $0.5\text{--}10\text{ mg L}^{-1}$ of Cu were released into the solutions in various reported Cu-based heterogeneous Fenton-like systems [23,24], which was much higher than the standard 1.3 mg L^{-1} of drinking water (National Primary Drinking Water Regulations, the United States). The Cu release might be inhibited by the chemical bonding of Cu in the structure of the catalyst.

In the present study, copper-doped mesoporous silica microspheres (Cu-MSMs) were synthesized by a hydrothermal method. The localized copper species in the structure of Cu-MSMs were characterized, and their catalytic performance was investigated by Fenton-like process. Phenytoin (PHT) is a representative antiepileptic drug. Chronic exposure to it can result in immune suppression and dermatosis even the concentration is low [25]. Ibuprofen (IBU), an anti-inflammatory drug, may alter the postembryonic development of anuran species in freshwater environs [26]. Diphenhydramine (DP) is the active ingredient of Benadryl, a first generation antihistamine drug that combines sedative, antiemetic, antitussive and hypnotic properties, and has shown

high toxicity with mutagenic and carcinogenic effects [27]. The three PhACs occurred extensively in the aquatic environment due to their high usage and their presence in wastewater [28]. Therefore, PHT, IBU and DP were selected to evaluate the activity and properties of the catalyst. The results indicated that the framework copper species in Cu-MSMs exhibited high efficiency and stability for the degradation of the PhACs in the presence of H_2O_2 at neutral pH values. A preliminary effort to identify the interaction process among the framework copper species of Cu-MSMs, PhACs and H_2O_2 has been undertaken.

2. Materials and methods

2.1. Materials and reagents

Two of the PhACs-DP and PHT were purchased from Acros (Geel, Belgium), and IBU was obtained from TCI Japan (Tokyo, Japan). Their purities were higher than 99%. Their molecular structures are shown in Fig. S1. Tetraethyl orthosilicate (TEOS), cetyltrimethyl ammonium bromide (CTAB), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2 , 30%, w/w), absolute ethanol and ammonia solution were purchased from Sinopharm Chemical Reagent Co. 5-Tert-butoxycarbonyl-5-methyl-1-pyrrolidine-N-oxide (BMPO) was provided by Dojindo Molecular Technologies. N,N-diethyl-p-phenylenediamine sulphate (DPD) and horseradish peroxidase (POD) were provided by Sigma Ltd. N,O-bis(Trimethylsilyl)trifluoroacetamide (BSTFA) was obtained from TCI Japan (Tokyo, Japan). All of the chemicals were at least of analytical grade. Deionized water was used throughout this study.

2.2. Catalyst preparation

Cu-MSMs were prepared using a hydrothermal method. Typically, 0.029 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 160 mL of deionized water to form solution A. Then, 1.8 g of CTAB was dissolved in 120 mL of absolute ethanol, and the mixed solution was stirred for 30 min to form solution B. Next, solution A was added to solution B, and the mixed solution was stirred for 30 min followed by addition of 4 mL of TEOS. After stirring for 1 h, 8 mL of ammonia (25 wt%) was added dropwise to the mixed system to form a sol. The synthesis medium was maintained under vigorous stirring for 6 h. Then, the sol was transferred to a Teflon-lined steel autoclave and heated to 100°C for 48 h. After natural cooling, the obtained product was filtered, washed with deionized water and dried at 100°C for 6 h. Finally, the crystallisation and template removal were carried out in a muffle furnace at a heating rate of 2°C/min to 550°C , which was maintained for 6 h. In addition, the content of copper in the sample was determined by ICP-OES (Optima 2000) after the sample was completely dissolved using nitric acid. By the same procedure, five samples with different copper content (0 wt%, 0.75 wt%, 0.93 wt%, 1.14 wt% and 1.55 wt%) were prepared, which were designated as M_0 , M_1 , M_2 , M_3 and M_4 , respectively. As a reference, iron-doped mesoporous silica microspheres (designated as M_{Fe}) was also synthesized as described above without the addition of the cupric nitrate but with the addition of ferric nitrate.

2.3. Characterization

The transmission electron microscopy (TEM) images of the samples were obtained using a JEOL-2010 TEM with an acceleration voltage of 200 kV. The scanning electron microscopy (SEM) images of the samples were obtained using a SU8020 FESEM (Hitachi). Nitrogen adsorption/desorption experiments of the samples were

carried out at -196°C using a Micromeritics ASAP2000 analyzer (Micromeritics, Norcross, GA). The samples were outgassed under a vacuum at 250°C for 4 h prior to conducting measurements. The specific surface areas were calculated from the isotherms using the BET method; and the pore-size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model. The powder X-ray diffraction (XRD) of the samples were recorded on a Scintag-XDS-2000 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$). The UV–vis diffuse reflectance spectroscopy (UV–vis DRS) were recorded on a Hitachi U-3900 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) data was taken on an AXIS-Ultra instrument (Kratos Analytical, UK) using monochromatic Al $\text{K}\alpha$ radiation (225 W, 15 mA, 15 kV). To compensate for surface charge effects, the binding energies were calibrated using the C1s hydrocarbon peak at 284.8 eV.

2.4. Procedures and analysis

Three PhACs (PHT, IBU and DP) were selected to evaluate the activity and properties of the catalyst. In a typical experiment, 50 mL of PhACs aqueous solution (10 mg L^{-1}) with neutral pH was placed in a beaker. A given amount of catalyst with equivalent Cu (0.058 mM) was added, and the suspension was stirred at room temperature for approximately 20 min to establish the adsorption/desorption equilibrium between PhACs and the catalyst. Then, a certain concentration of H_2O_2 was added to the above suspensions under continuous stirring. The optimal dosages of H_2O_2 (10 mM) were determined according to the best activity of PHT degradation under otherwise identical conditions (Fig. S2), and used in all the experiments unless specific illustration. Then, samples were taken at set intervals using a 1 mL syringe, filtered immediately through a $0.45 \mu\text{m}$ Millipore filter. The filtered liquor and the solid residues on the surface of the filter were collected for further analysis. All the pollutants were analyzed by means of a 1200 series HPLC (Agilent, U.S.A.) equipped with a UV detector and a ZORBAX Eclipse XDB-C₁₈ column ($4.6 \times 150 \text{ mm}$, $5 \mu\text{m}$). The mobile phase was a 60/40% (v/v) mixture of acetonitrile/water with a flow rate of 1 mL min^{-1} . TOC was determined by a Shimadzu TOC-V_{CPH} analyzer. The released metallic ions from the catalysts in reaction process were determined by ICP-OES on an OPTIMA 2000 (Perkin Elmer Co., U.S.A.). The H_2O_2 concentration was determined using a DPD method according to a previously published procedure [29]. To test the stability and recyclability of the catalysts, the materials were filtered, washed with water, and dried at 100°C . The catalysts were used in the following cycle. All information for the samples preparation and measurements of electron spin resonance (ESR), gas chromatography–mass spectrometry (GC–MS), Fourier-transform infrared spectra (FTIR) and *in situ* Raman spectra were shown in Supporting information. Each experiment was run in triplicate. Data were the arithmetic mean of three measured values.

3. Results and discussion

3.1. Characterization of catalysts

The properties of the synthesized Cu-MSMs samples with various Cu contents determined by ICP-OES were included in Table 1. Fig. 1a and b shows the typical SEM images of the silica microspheres, revealing that both the pure mesoporous silica microspheres (M_0) and copper-doped mesoporous silica microspheres (M_2) were spherical with a narrow range of size distribution and an average diameter of $500 \text{ nm} \pm 20 \text{ nm}$. M_2 had a more perfect spherical shape than M_0 , indicating that the introduction of copper to the framework of mesoporous silica was in favor of the formation of microspheres. Fig. 1c and d displays the TEM images of M_0 and M_2 , suggesting that Cu-MSMs had a multiporous structure. The porous properties of the samples were further obtained from N_2 adsorption–desorption measurements (Fig. S3). Both M_0 and M_2 exhibited the adsorption–desorption isotherms of type IV with hysteresis loops, large surface areas of 1063.4 and $1026.5 \text{ m}^2 \text{ g}^{-1}$, and narrow pore diameters of 2.33 nm and 2.36 nm , respectively, indicating that Cu-MSMs had the typical mesoporous structure. The XRD patterns of all the synthesized samples are shown in Fig. 2. In the low-angle range, all of the samples exhibited the (100) diffraction peak, which was assigned to pure mesoporous silica, indicating that the mesoporous structure did not collapse upon introduction of copper. In the high-angle XRD patterns, the broad peak at 23° corresponded to amorphous silica, and no diffraction peaks of copper oxide (CuO_x) were observed in these samples, indicating that the small amounts of copper species might be highly dispersed in the structure or do not form the crystals of CuO_x [23]. On the other hand, the unit cell parameter (a_0) increased with the order of $\text{M}_0 < \text{M}_1 < \text{M}_2$ and reached an upper limit of 4.27 when the copper content increased to $0.93 \text{ wt\%}$ (M_2) in the structure of the materials as shown in Table 1, indicating that Cu^{2+} was incorporated into the framework of the materials to replace Si^{4+} due to the larger ionic radius of Cu^{2+} compared to that of Si^{4+} [30]. However, the a_0 did not increase significantly as copper content increased to $1.14 \text{ wt\%}$ (M_3) and $1.55 \text{ wt\%}$ (M_4), suggesting that there existed an upper limit of the amount of copper that could be incorporated inside the framework, and a further increase in the copper content would lead to the presence of extraframework copper species.

The metallic states of the copper species in Cu-MSMs were measured semi-quantitatively by UV–vis DRS (Fig. 3). All of the samples exhibited strong absorption peaks at ca. 220 nm and 255 nm , which corresponded to the charge transfer transitions of isolated Cu(II) in coordination with lattice oxygen [31,32]. This result suggested the formation of Si-O-Cu in the framework of the samples [30,33,34]. In addition, both M_3 and M_4 exhibited two peaks in 300 and $600\text{--}800 \text{ nm}$ regions which did not appear in the spectra of M_1 and M_2 , indicating that the excess copper showed the different existence state. The absorption bands at 300 nm corresponded to the charge transfer between the Cu(II) and oxygen in the $[\text{Cu-O-Cu}]_n$ surface species, which contributed to the extraframework copper oligomers or aggregated copper oxide clusters [35,36]. The broad absorption bands in the region of $600\text{--}800 \text{ nm}$ were assigned to the d–d transition of Cu(II) in the pseudo-octahedral ligand field generated by oxygen ions, indicating the presence of extraframework CuO particles [35]. Based on the analysis above, the distribution percentages of the framework copper and extraframework copper of different catalysts were presented in Table 1. The copper species of M_1 and M_2 were primarily in the framework (approximately 98% in the total copper), and the amount of the framework Cu calculated by the Cu contents of Cu-MSMs multiplied by the percentages of the framework Cu were

Table 1
Properties of the synthesized samples.

Sample	Cu content (wt%)	Framework Cu ^a (%)	Extraframework Cu ^b (%)	d (100) (nm)	a_0^c (nm)
M_0	0	0	0	3.52	4.06
M_1	0.75	98.53	1.47	3.57	4.12
M_2	0.93	97.47	2.53	3.70	4.27
M_3	1.14	79.19	20.81	3.64	4.20
M_4	1.55	58.94	41.06	3.71	4.28

^a The percentages of framework species in total copper.

^b The percentages of extraframework species in total copper.

^c Unit cell parameter.

Fig. 1. Morphologies of the mesoporous silica microspheres and copper-doped mesoporous silica microspheres (Cu-MSMs): (a) SEM image of M_0 ; (b) SEM image of M_2 ; (c) TEM image of M_0 ; and (d) TEM image of M_2 .

Fig. 2. XRD patterns of the synthesized samples. Insert shows the corresponding high-angle XRD patterns.

0.74 wt% and 0.91 wt%, respectively. However, the amount of the framework Cu in M_3 and M_4 were 0.90 wt% and 0.91 wt%, and the amount of their extraframework Cu calculated by the Cu contents multiplied by the percentages of the extraframework Cu were 0.24 wt% and 0.64 wt%, respectively. The results indicated that the copper species with an upper limit of 0.91 wt% existed in the framework of Cu-MSMs, and above the upper limit, the copper species were primarily located in the extraframework sites, which agreed with the results of XRD.

The presence of Cu(I) and Cu(II) on the surface of Cu-MSMs was confirmed using the XPS measurement, as shown in Fig. 4. The peaks of M_2 corresponding to Cu $2p_{3/2}$ were observed at ca. 933.7 and 935.6 eV for reduced copper species and Cu(II) [37], respectively. Cu(II) was also observed due to the appearance of a shake-up satellite line at ca. 943.9 eV. The Auger parameter at 1847.8 eV confirmed the existence of Cu(I). It should be noted that the Cu $2p_{3/2}$ binding energy (935.6 eV) for Cu(II) was much higher than that for pure CuO (~933.8 eV) [38], indicating that the high

electron affinity of silicon resulted in the movement of electrons from copper to silicon [39]. This evidence further supported the formation of Si—O—Cu in the framework of the samples. Similarly, Cu(I) and Cu(II) were also detected on the surface of M_4 . In addition, the peak fitting of the O 1s spectra for M_2 and M_4 were shown in Fig. S4. The first peak, P_1 in the 532.5–533.5 eV range was the O 1s peak that characterized the lattice oxygen; and the second peak, P_2 in the range of 533.5–534.5 eV that denoted O 1s lateral structure. The oxygen vacancy concentration could be calculated from the variation of area ratio R of the two O 1s peaks [40]. The value of $R(M_2)$ 7.78 was higher than that of $R(M_4)$ 6.42, indicating that the oxygen vacancy concentration of M_4 was higher than that of M_2 , which was attributed to the extraframework copper species in M_4 .

3.2. Degradation of PhACs in Cu-MSMs suspensions with H_2O_2

According to the given amount of catalyst with equivalent Cu (0.058 mM), the Fenton-like catalytic activity of the different catalysts were evaluated by the degradation of PHT with H_2O_2 as shown in Fig. 5. During the adsorption/desorption equilibrium, only about 10% of the PHT were adsorbed for all the samples. After adding H_2O_2 , no significant degradation of PHT was observed in the M_0 suspension, and only 22.6% of PHT was degraded in the M_{Fe} (iron-doped mesoporous silica microspheres) suspension within 120 min. However, PHT was substantially degraded in the Cu-MSMs suspensions. The PHT conversion at 60 min followed the order of M_0 (8.4%) < M_{Fe} (13.0%) < M_4 (80.0%) < M_3 (83.4%) < M_1 (94.4%) < M_2 (96.0%). The TOC removal at 180 min followed the order of M_4 (43.7%) < M_3 (48.3%) < M_1 (56.3%) < M_2 (62.6%). According to the previously described method (SI) [41], the utilization efficiency of H_2O_2 was defined as the ratio of the stoichiometric amount of H_2O_2 for the mineralization of pollutants to the total amount of the really consumed H_2O_2 in the reaction, and this value followed the order of M_4 (63.4%) < M_3 (71.9%) < M_1 (82.9%) < M_2 (84.0%) at the time of the initial PHT disappeared. M_1 and M_2 where the copper species were primarily in the

Fig. 3. Deconvoluted subbands in the UV-vis DRS of the synthesized samples with different amounts of copper. Inset shows the relative UV-vis DRS.

Fig. 4. XPS spectra in Cu 2p_{3/2} for M₂ and M₄. Inset shows the LMM X-ray induced Auger parameter for the corresponding sample.

framework exhibited the best activity and the highest utilization efficiency of H₂O₂, while M₃ and M₄ with considerable extraframework copper species exhibited lower activity and utilization efficiency of H₂O₂.

In addition, the degradation of other two PhACs (IBU and DP) had the same regularities (Fig. 6). M₂ exhibited the best activity during IBU and DP degradation and they could be completely converted within 120 min and 90 min, respectively, while M₃ and M₄ exhibited a lower activity. At 180 min of reaction, the TOC removal of IBU and DP in M₂ suspensions were 61.3% and 64.5%, respectively, while in M₃ and M₄ suspensions, the TOC removal were below 50%. The utilization efficiency of H₂O₂ at the time of the initial IBU and DP disappeared followed the order of M₄ (58.1%) < M₃ (72.9%) < M₂ (83.7%), and M₄ (59.2%) < M₃ (64.3%) < M₂ (80.8%), respectively. These results suggested that the copper species in the framework were more efficient than the ones in the

Fig. 5. Fenton-like degradation of PHT under different suspensions: (a) M₀ (0.4 g L⁻¹); (b) M_{Fe}; (c) M₁; (d) M₂; (e) M₃; and (f) M₄. (Initial PHT 10 mg L⁻¹, initial H₂O₂ 10 mmol L⁻¹, equivalent metal 0.058 mmol L⁻¹.)

Fig. 6. Fenton-like degradation of IBU (A) and DP (B) under different suspensions: (a) M_0 (0.4 g L^{-1}); (b) M_2 ; (c) M_3 ; and (d) M_4 . (Initial PhACs 10 mg L^{-1} , initial H_2O_2 10 mmol L^{-1} , equivalent Cu $0.058 \text{ mmol L}^{-1}$.)

extraframework of Cu-MSMs for the Fenton-like degradation of PhACs.

The stability tests of Cu-MSMs were carried out by PHT degradation. At the end of reaction, the amount of copper leaching had the order of M_1 (0.16 mg L^{-1}) < M_2 (0.17 mg L^{-1}) < M_3 (0.40 mg L^{-1}) < M_4 (0.47 mg L^{-1}), suggesting that the extraframework copper species leached into the solution more easily than the framework copper species during the Fenton-like reactions. To investigate the effect of dissolved metal ions on degradation, a homogeneous experiment using 0.2 mg L^{-1} Cu(II) with 10 mM H_2O_2 was conducted and got only 6.5% of the TOC abatement within 180 min, indicating that the observed PhACs removals in the M_1 and M_2 suspensions were mainly attributed to heterogeneous catalytic reactions. In addition, the activity of M_2 did not markedly decrease after six successive cycles of degradation testing (Fig. S5), and it was observed that the Cu(II) leaching from Cu-MSMs became fewer and fewer, less than 0.1 mg L^{-1} with the cycling times. The results suggested that M_2 was an effective and stable catalyst for heterogeneous Fenton reactions.

3.3. Role of the framework copper species in Cu-MSMs on Fenton-like process

A series of H_2O_2 decomposition experiments were performed in the presence of Cu-MSMs without PhACs (Fig. 7) where H_2O_2 finally decomposed into O_2 . The decomposition rate had the order of $M_1 < M_2 < M_3 < M_4$, suggesting that these catalysts exhibited the opposite reactivity for the decomposition of H_2O_2 compared to the degradation of PhACs, and the rate of H_2O_2 disappearance increased with increasing the ratio of extraframework copper in Cu-MSMs. M_2 exhibited the highest catalytic activity toward the PhACs degradation and lower activity for the H_2O_2 decomposition,

Fig. 7. H_2O_2 decomposition under different suspensions. (Initial H_2O_2 10 mmol L^{-1} , equivalent Cu 0.058 mM .)

indicating that the framework copper species in Cu-MSMs were extremely selective for promoting Fenton chemistry with minor spurious decomposition of H_2O_2 to O_2 . Since oxygen vacancies took part in the decomposition of H_2O_2 into O_2 [42], M_4 showed the highest activity for the decomposition of H_2O_2 due to its higher concentration of oxygen vacancies, which were produced by the extraframework copper species in the form of aggregated copper oxide clusters. In our previous study [43], no $\cdot\text{OH}$ formation was determined with the decomposition of H_2O_2 in aqueous CuO_x - H_2O_2 suspension, confirming this mechanism.

The ESR spin-trapping technique (with BMPO) was employed to detect the reactive oxygen species (ROS) involved in the suspension of the catalyst with H_2O_2 . As shown in Fig. 8, no significant signals were attributed to $\cdot\text{OH}$ in the control experiments without catalyst (curve a) or in the M_0 aqueous dispersion (curve b), while four characteristic peaks of BMPO- $\cdot\text{OH}$ were observed in the aqueous dispersion of Cu-MSMs with H_2O_2 (curve c–f). The intensities of these peaks in the suspension with H_2O_2 had the sequence: $M_2 > M_1 > M_3 > M_4$. The formation of HO_2/O_2^- radicals was also detected in methanol, and the similar rule with the formation of $\cdot\text{OH}$ radicals was found in the systems. The result was in agreement with the catalytic activity of Cu-MSMs for the degradation of PhACs, indicating that H_2O_2 was more effectively converted to $\cdot\text{OH}$ and HO_2/O_2^- radicals at the interface of M_2 where the copper species were primarily in the framework of Cu-MSMs.

3.4. Role of the intermediates from PhACs degradation in M_2 suspension

GC-MS was used to monitor the generation of reaction intermediates during the degradation of PhACs in M_2 suspension. All of the identified compounds were unequivocally identified using the NIST98 library database with fit values higher than 90%. Table S1a shows the main intermediates from the degradation of PHT at 20 min reaction time. 5 aromatic products, including 4-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 2-(3,4-dihydroxyphenyl)-2-hydroxyacetic acid, 2-(3,4-dihydroxyphenyl)-2-hydroxyethylamine and PHT, and 2 low-molecule weight organic acids were detected on the surface of M_2 , whereas 6 alcohols, 2 aromatic products including benzoic acid and PHT were detected in the solution. These results indicated that the degradation of PHT and intermediates predominantly occurred on the surface of M_2 . For other two PhACs, there were almost the same regularities of the intermediates distribution as PHT degradation. As shown in Table S1b and c, except for some low-molecule weight organics, several aromatic products including 2-(3,4-dihydroxyphenyl)-2-hydroxyacetic acid, benzoic acid, 4-hydroxybenzoic acid, 2,4-

Fig. 8. BMPO spin trapping ESR spectra recorded at ambient temperature for the synthesized samples as catalysts (A) in an aqueous dispersion for BMPO-OH and (B) in a methanol dispersion for BMPO-HO₂/O₂⁻: (a) H₂O₂; (b) H₂O₂ with M₀; (c) H₂O₂ with M₁; (d) H₂O₂ with M₂; (e) H₂O₂ with M₃; and (f) H₂O₂ with M₄.

dihydroxybenzoic acid, 1,4-benzenedicarboxylic acid and diphenylmethanol were detected during the degradation of IBU and DP, respectively. These aromatic intermediates were found only on the surface of M₂, and were not found in the solutions, except for benzoic acid, indicating that the aromatic intermediates were predominantly adsorbed on the surface of the catalyst. Moreover, most of the intermediates are acids and alcohols, and more likely to be further treatment, indicating that the deleterious effect for the environment of the initial PhACs were significantly weakened. Because the tested compounds showed similar degradation courses, PHT was used in the following investigation unless specified otherwise.

To elucidate the surface reaction process, the samples of PHT, M₀ and M₂ from different reaction times were filtered and dried for FTIR measurement (Fig. 9). The spectra of M₀ displayed a wide absorption band at 3335 cm⁻¹, ascribed to the stretching vibrations of OH [ν(OH)] on the surface of M₀ [23]. With incorporating framework copper species (M₂), the intensity of the band significantly increased, indicating that ν(OH) was closely related to the framework copper species. According to Tamura et al. [44], metal oxide species in aqueous solution could form surface hydroxyl groups by dissociative chemisorptions of water molecules. The incorporation of framework copper in mesoporous silica increased the concentration of the surface unsaturated Cu centers, increasing the intensity of ν(OH). For PHT compound, the absorption bands at 3271 and 3207 cm⁻¹ ascribed to the stretching vibration of N—H, the band at 1774 and 1718 cm⁻¹ were assigned to the stretching vibration of C=O, and the bands at 1448 and 1402 cm⁻¹ were assigned to the skeleton vibration of aromatic rings [45]. There were no significant changes between the spectra of M₂ used after

Fig. 9. FTIR spectra for various samples: (a) PHT; (b) M₀; (c) fresh M₂; (d) M₂ used after 20 min adsorption of PHT; (e) M₂ used after 20 min Fenton reaction of PHT; (f) M₂ used after 60 min Fenton reaction of PHT; and (g) M₂ used after 300 min Fenton reaction of PHT.

20 min adsorption of PHT and the spectra of fresh M₂, indicating that PHT was not copiously adsorbed on the surface of M₂, due to no —OH or —COOH existing in the structure of PHT. However, after adding H₂O₂ and maintaining Fenton-like reaction 20 min, the intensity of the band of ν(OH) further increased and the centroid of this band shifted to 3283 cm⁻¹. According to the result of GC-MS measurement, many phenolic intermediates, such as 4-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid and 2-(3,4-dihydroxyphenyl)-2-hydroxyacetic acid, were on the surface of M₂ at this time. The increase of the —OH group on the surface caused the enhancement of the band of ν(OH). The shifted of this band was contributed by the deprotonation of the phenolic OH group of the intermediates and different surroundings in the first coordination sphere of the Cu²⁺ [45]. This result indicated that the phenolic intermediates complexed with the surface Cu of M₂ by σ bonding to the lone pairs of oxygen atom of the phenolic OH group, namely, ≡Cu-ligands complexes [46]. The appearance of the organic absorption bands at 1774, 1718, 1448 and 1402 cm⁻¹ validated this result. Afterwards, the band of ν(OH) changed into 3396 cm⁻¹ at 60 min Fenton-like reaction and the organic absorption bands between 1400 and 1800 cm⁻¹ weakened, suggesting that the organic pollutants were continuously degraded and the new aromatic intermediates adsorbed on the catalyst, forming new ≡Cu-ligands complexes, leading to the continuous change of the chemical surroundings. After 300 min reaction, all bands for organic compound disappeared, the band of ν(OH) shifted to 3335 cm⁻¹ again, indicating that the ≡Cu-ligands complex completely disappeared with the degradation of the organics.

Furthermore, the interaction processes among PHT, M₂ and H₂O₂ were observed by *in situ* Raman spectra. As shown in Fig. 10, no any special band appeared in the M₂ suspension, while two bands at 475 and 820 cm⁻¹ appeared in the PHT/M₂ suspension, which were assigned to the ring wagging and aromatic C—H twisting of PHT, respectively [47]. The spectra of the M₂/H₂O₂ suspension displayed a significant peak at 880 cm⁻¹ associated with the O—O stretching vibration [48], indicating that H₂O₂ was physisorbed onto the channel in M₂. In the PHT/M₂/H₂O₂ suspension, the bands at 475 and 820 cm⁻¹ did not appear, indicating that the structure of PHT was destroyed by Fenton-like process. The band at 880 cm⁻¹ weakened and a new organic band at 578 cm⁻¹ ascribed to C—O rocking appeared [47], indicating that there was a competitive adsorption between H₂O₂ and the generated intermediates on the surface of M₂ during the Fenton-like process.

Moreover, it was found that the surface concentration ratio of Cu⁺ to Cu²⁺ was approximately 3.2:1 on the surface of M₂ after

Fig. 10. *In situ* Raman spectra for various suspensions: (a) M_2 ; (b) PHT/ M_2 ; (c) M_2/H_2O_2 ; and (d) PHT/ M_2/H_2O_2 .

60 min of reaction during the PHT degradation, more than the 2:1 ratio before the reaction by XPS analysis (Fig. S6). The results suggested that the interaction of $\equiv Cu$ -ligands and H_2O_2 promoted the generation of Cu(I), overcoming the rate-limiting step of the reduction of $M^{(n+m)+}$ to M^{n+} in Fenton-like process and accelerating the Cu(II)/Cu(I) cycles on the surface of Cu-MSMs for the degradation of PhACs.

On the basis of all the above information, a possible interaction process among the framework copper species of Cu-MSMs, PhACs and H_2O_2 was proposed. During the Fenton-like catalytic degradation of PhACs, H_2O_2 was reduced by Cu(I) to generate $\cdot OH$ and Cu(II) [49]. The hydrocarbon groups on the aromatic ring of PhACs were firstly attacked by $\cdot OH$ to form benzoic acid. Then the hydroxylation reaction occurred on the aromatic ring at the para/ortho-position of the carboxyl group to form monohydroxy or dihydroxy aromatic substances, such as 4-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid and 2-(3,4-dihydroxyphenyl)-2-hydroxyacetic acid. Most of produced phenolic intermediates were adsorbed on the surface of Cu-MSMs, complexing with the framework $\equiv Cu(II)$ species, forming $\equiv Cu$ -ligands. $\equiv Cu$ -ligands then interacted with H_2O_2 , enhanced the reduction rate of $\equiv Cu(II)$, resulting in the more $\equiv Cu(I)$ production, and consequently accelerated the Cu(II)/Cu(I) cycles on the surface of the catalyst, leading to more $\cdot OH$ generation for the PhACs oxidation.

4. Conclusions

Cu-MSMs with the coexistence of Cu(I) and Cu(II) were synthesized by a hydrothermal method. The copper species with an upper limit of 0.91 wt% existed in the framework of Cu-MSMs, and above the upper limit the copper species were primarily located in the extraframework sites, leading to more oxygen vacancies on the surface of Cu-MSMs. M_2 with 0.93 wt% of Cu, possessing the maximum framework copper content, exhibited the highest catalytic efficiency and stability for the degradation of PhACs in the presence of H_2O_2 under neutral condition. In the M_2/H_2O_2 system, the conversion of PHT, IBU and DP could reach 100% within 75 min, 120 min and 90 min, respectively; and the leaching of Cu were below 0.2 mg L^{-1} , much lower than the EU directives ($<2 \text{ mg L}^{-1}$) and USA regulations ($<1.3 \text{ mg L}^{-1}$). During the heterogeneous Fenton-like process, the framework $\equiv Cu(I)$ in Cu-MSMs primarily converted H_2O_2 into $\cdot OH$, and $\equiv Cu(I)$ was oxidized to $\equiv Cu(II)$ by H_2O_2 in the H_2O_2 reduction semi-reaction. Meanwhile, in the H_2O_2 oxidation semi-reaction, most of produced phenolic intermediates were adsorbed on the surface of Cu-MSMs, complexing with the framework $\equiv Cu(II)$, forming $\equiv Cu$ -ligands. $\equiv Cu$ -ligands then interacted with H_2O_2 and enhanced the reduction rate of the framework $\equiv Cu(II)$, resulting in the more $\equiv Cu(I)$

production, overcoming the rate-limiting step of the reduction of $M^{(n+m)+}$ to M^{n+} in Fenton-like process; consequently accelerated the Cu(II)/Cu(I) cycles on the surface of the catalyst, leading to more $\cdot OH$ generation for the PhACs oxidation. The synergic effect of generated ligands and the framework copper species in the mesoporous silica microspheres resulted in the enhanced catalytic activity of Cu-MSMs under neutral condition. Although the Cu-ligand complexes-associated mechanism needs further in-depth study, these results are encouraging for the rational design of new heterogeneous Fenton catalysts and the application of ligands-driven Fenton process under neutral condition.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21407165, 21125731, 51138009, 51278527).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.03.137>.

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