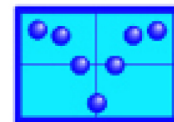
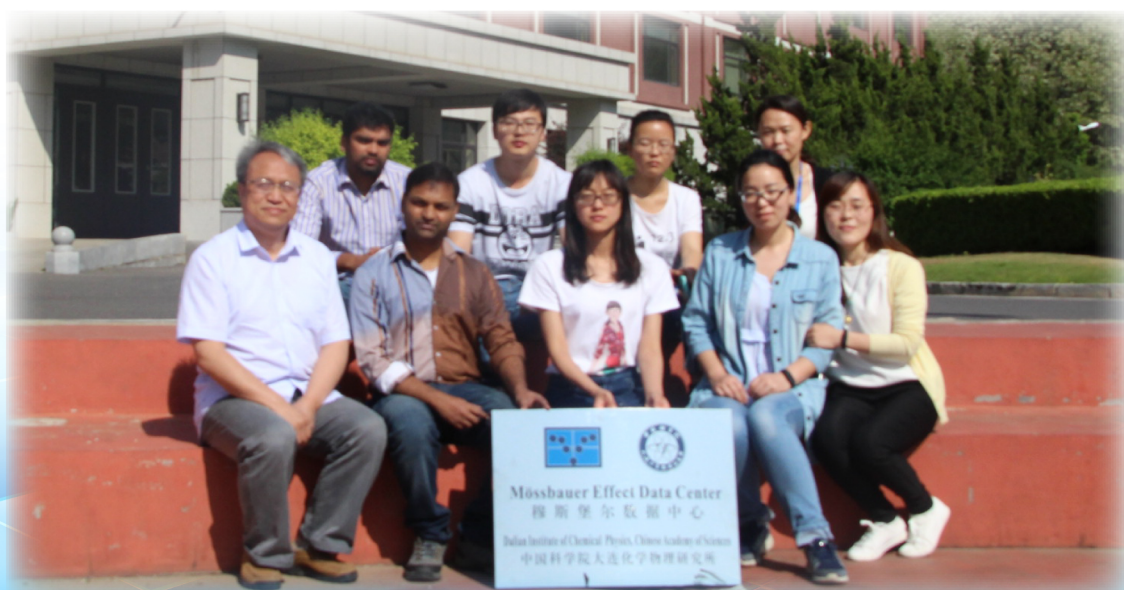
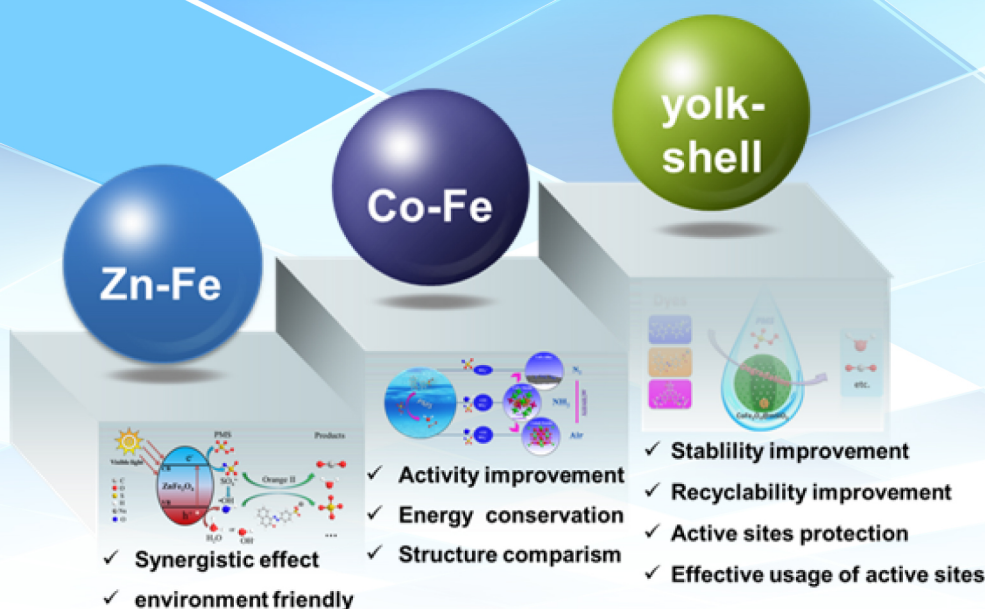


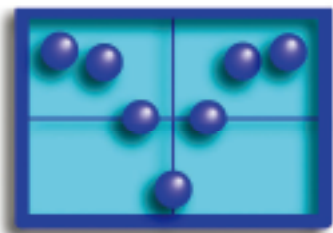
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Application of Mössbauer spectroscopy in iron-based nanocomposites for catalytic peroxymonosulfate activation

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Abstract

Prof. Junhu Wang's team in the Mössbauer Effect Data Center have made a series of investigation on the synthesis and characterization of different kinds of iron-based nanocomposites by advanced techniques. Herein, we made a mini review on the design of different cobalt-iron nanocomposites, such as zinc ferrites, cobalt ferrites, cobalt-iron alloys, etc., and their application in the catalytic activation of peroxymonosulfate (PMS) for organic pollutants degradation in wastewater treatment.



Kaixin Zhu has just obtained her doctor's degree in Industrial Catalysis at Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Her PhD thesis focused on the topic: Preparation of Iron-contained Catalysts Based on Peroxymonosulfate Activation for

Pollutants Degradation. She has published several papers on the synthesis of iron-based nanocomposites and their catalytic efficacy on peroxymonosulfate (PMS) activation for organic pollutants degradation, such as Catal. Sci. Technol., Catal. Lett., Catalysts, and so on.



Junhu Wang is a Professor of Chemistry, main research fields are Mössbauer spectroscopic applications and nanometer catalytic materials. He was graduated from Radiochemistry Major, Lanzhou University in 1991. He was awarded the master's and doctor's degrees (jointly trained with Japan Atomic Energy Research Institute) of Toho University (Japan) in 1998 and 2002, respectively. He holds many titles and awards, such as full professor & group leader of Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS), winner of "Hundred Talents Program" honor of introducing outstanding talents from abroad and the financial incentives, Secretary-general of Mössbauer Effect Data Center (MEDC), Executive Editor of Mössbauer Effect Reference and Data Journal (MERDJ), Executive Chairman of 8th International Symposium on the Industrial Applications of the Mössbauer Effect, Member of Councils of China Nuclear Physics Society (CNPS) and Chinese Mössbauer Community, Advisor Member of International Board on the Applications of

the Mössbauer Effect (IBAME), Members of American Chemical Society (ACS) and Chinese Chemical Society (CCS). Over the years, he served at Tokyo National University of Fine Arts and Music (Japan), National Institute for Materials Science (NIMS), National Institute of Advanced Industrial Science and Technology (AIST), and Chukyo University for scientific research and teaching, during which he engaged in researches on Mössbauer spectroscopic studies on structural chemistry of lanthanide and actinide element compounds, hydrogen generation from photocatalytic water splitting over oxide semiconductors, pollutants degradation and mineralization with hydroxyapatite (HAP)/titania nanocomposited photocatalysts, spectroscopic studies on heterogeneously nanocomposites and cation/anion codoped novel titanium oxide photo-catalytic materials, surface chemistry of phosphate-base catalytic materials, highly active and anti-sinter HAP supported gold catalysts, shape-controlled synthesis of noble metal and composite oxide based electrocatalytic materials, Prussian blue analogues (PBAs) and spinel double oxides developments for removing pollutants in water as well as reactive adsorption materials for fuel-desulfurization and toxic metal ions purification. Current Research Interests: 1) Novel and highly efficient environmental & energy catalytic materials; 2) Novel and highly efficient reactive adsorption materials; and 3) The development and applications of in-situ advanced spectroscopic techniques.

Introduction

The refractory organic pollutants from different industries such as dyes, plastics, pharmaceuticals, rubber, cosmetics, etc., have attracted great attention in the field of wastewater treatment [1-4]. Apart from the traditional advanced oxidation processes based on the hydroxyl radicals ($\bullet\text{OH}$), the novel sulfate radical based advanced oxidation processes (SR-AOPs), especially in PMS (a new chemical oxidant) activation have been widely studied during the last decade, due to its properties of stable, environmentally friendly, easy to store and transport, high efficient, etc. [5]. In general, PMS can be activated by heat, UV, ultrasound, and transitional metals (Co, Cu, Mn, etc.) to produce strong oxidized sulfate radicals, which is highly efficient in organic pollutants degradation. Among all the heterogeneous catalysts for PMS activation,

ferrites [6-8], as well as other iron-contained nanomaterials [9, 10] were popular and attractive catalysts taking advantages of easy recovery, high efficiency, and good stability. CuFe_2O_4 was reported to perform higher activity and lower ion leaching than CuO , which was resulted from the higher stability of bimetal spinel structure of the copper ferrites [11]. Iron-cobalt mixed oxides catalyst was more efficient than Co_3O_4 , Fe_2O_3 , as well as their mechanical mixture, since the coexistence of Fe and Co could obtain synergistic effect of the formation of hydroxyl groups and fast electron transfer on the Fe-Co catalyst surface [12]. Even so, further studies still needed to be explored on the mechanisms of the ferrites in PMS catalytic activation, efficacy differences in catalysts prepared by different methods, optimal design of more efficient catalysts, and so on.

These features of iron-based catalysts in PMS activation, have promoted us on the further study in its mechanisms exploration and materials design, especially applied advanced Mössbauer spectroscopy in the characterization of iron-based catalysts. In our research, zinc ferrite was prepared through an extended soft chemical solution process (SCSP) [13, 14], and applied in the activation of PMS for Orange II degradation under visible light [15]. Furthermore, different kinds of cobalt-iron compounds (alloys, oxides, nitrides) were obtained under different calcination atmospheres (nitrogen, air, ammonia), which were verified by the Mössbauer spectra and XRD patterns [16]. In addition, from the point view of active sites protection and effective utilization, yolk/shell cobalt ferrite/mesoporous silica (mSiO_2) catalyst with well-defined architecture was synthesized by a hard-templating method, in which higher efficiency, better stability and recyclability than the conventional supported catalyst and naked cobalt ferrite without mSiO_2 were obtained [17]. The preparation of different kinds of iron-based catalysts, the structure characterization of the fresh and used catalysts by Mössbauer spectroscopy will be reviewed in this paper.

1. Synergism of zinc ferrite/PMS/visible-light system for organic pollutants degradation

1.1 Synthesis of zinc ferrite

The zinc ferrite was prepared through a method of SCSP. Typically, $\text{Zn}(\text{acac})_2$ and

$\text{Fe}(\text{acac})_3$ (molar ratio 1:2) were used as precursors, and 2-ethoxyethanol acted as solvent. After dissolution, H_2O_2 was added into the solution under magnetic stirring. After drying at 120 °C, the catalysts were obtained by calcination at different temperatures for 4 h in air. Hereafter, the prepared zinc ferrite samples were denoted as ZnFe-T , where T represents the final thermal treatment temperature of 300, 500, 700 and 900 °C.

1.2 Structure characterization and stability determination

After combining with the results from TG analysis and XRD patterns, stable zinc ferrites were confirmed to be obtained after calcination at higher than 500 °C. Mössbauer spectra were applied to characterize the state of iron in the prepared samples under different calcination temperatures, shown in **Figure 1**. Similar doublet

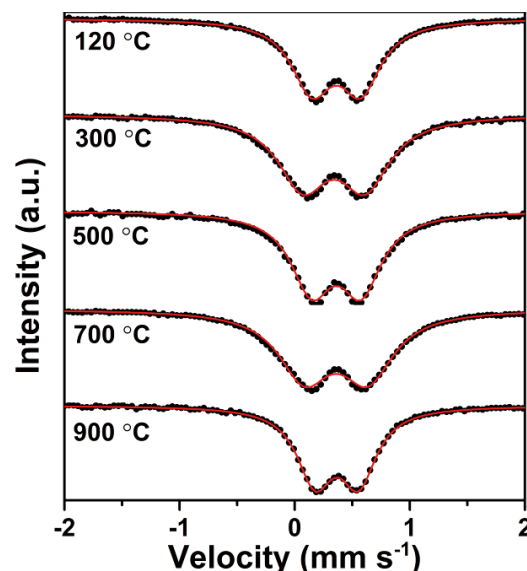


Figure 1. Mössbauer spectra of zinc ferrites calcined at different temperatures.

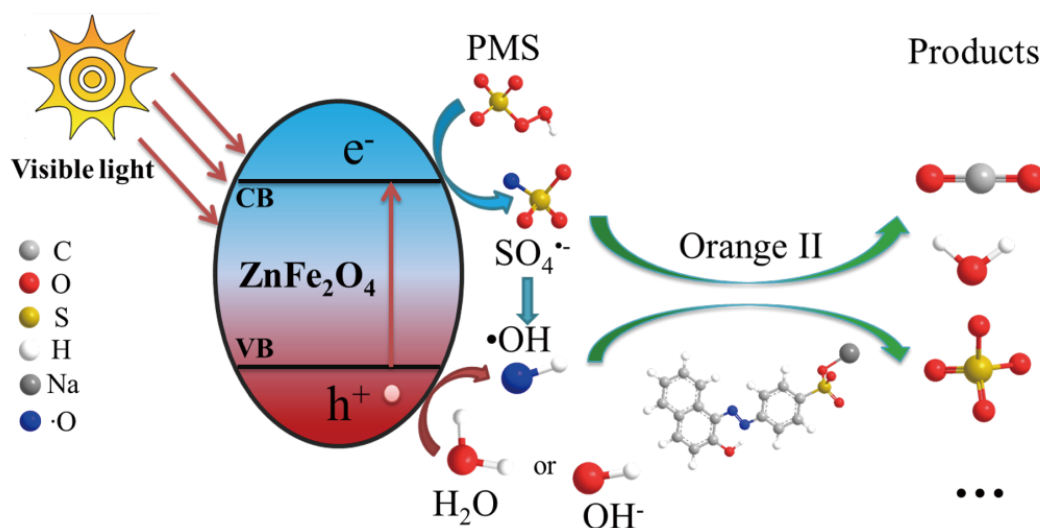


Figure 2. Proposed mechanism photocatalysis/PMS coupled system on zinc ferrite catalyst.

with IS (isomer shift), QS (quadrupole splitting), and line width at 0.34 ~ 0.36 mm s⁻¹, 0.38 ~ 0.55 mm s⁻¹, and 0.38 ~ 0.55 mm s⁻¹, respectively, clearly demonstrated the formation of spinel zinc ferrites excluding the presence of iron oxides.

Taking ZnFe-500 as catalysts for PMS activation in Orange II degradation under visible light irradiation, synergistic effects were proposed to exist between ZnFe-500 , PMS and visible light. It was reported that almost total decolorization was realized during the tested 80 min in the integrated system, however, the Orange II solution could not be

significantly removed in the system that lacked of either one (ZnFe-500 with PMS, ZnFe-500 with visible light, and PMS with visible light). Thus, the reaction mechanism was predicted as the scheme in **Figure 2**. ZnFe-500 acting as a semiconductor can be induced by visible light. Through irradiation, electrons were excited from the valence band to the conduction band, leaving the corresponding holes in the valence band simultaneously. Then, the photoinduced electrons could migrate to the catalyst surface and then be captured by PMS. As a result, PMS was activated by the photoinduced electrons to produce $\text{SO}_4^{\bullet-}$. On the other hand,

the photoinduced holes can react with surface-adsorbed H_2O or OH^- to produce $\bullet\text{OH}$. Both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ acted as the main species for oxidizing Orange II pollutant into CO_2 , H_2O or other inorganic molecules. The above processes made the separation efficiency of photoinduced electron-hole pairs be effectively improved; the Orange II degradation activity was efficiently enhanced.

Mössbauer spectra (Figure 3) of the fresh and used ZnFe-500 showed no variation in the doublet, indicating the good stability of zinc ferrite in the ZnFe-500/PMS/vis system.

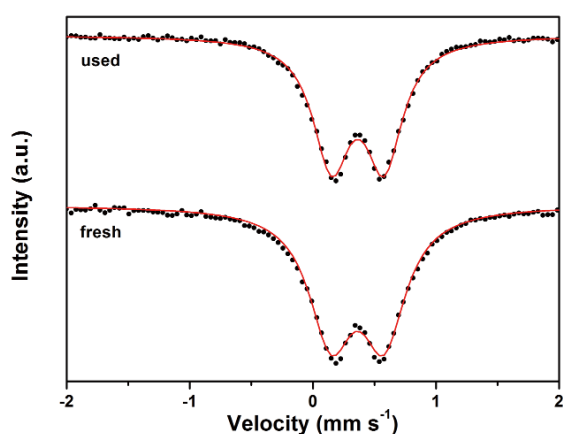


Figure 3. Mössbauer spectra of ZnFe-500 before and after reaction.

2. Comparison study on different kinds of cobalt-iron nanomaterials

2.1 Synthesis of different cobalt-iron nanomaterials

Co/Fe-based catalysts were prepared through an extended soft chemical solution process reported previously. Differently, the catalysts were obtained by calcination under special atmosphere. The prepared cobalt-iron samples are denoted as CFX-*T*, where *X* represents the calcination atmosphere of air (A), nitrogen (N) and ammonia (NH) and *T* represents the final calcination temperature (500 or 600 °C).

2.2 Structure determination

In order to exam the local environment of iron in different catalysts, all the synthesized cobalt-iron nanomaterials were characterized by Mössbauer spectroscopy. As shown in Figure 4, the six samples clearly presented different room temperature (RT) ^{57}Fe Mössbauer spectra together with their fit. The spectra of CFA-500 and CFA-600 (Figure 4a,

b) mainly displayed the presence of Fe^{3+} in the CoFe_2O_4 spinel phase with a partial degree of inversion. CoFe_2O_4 was known to prefer to form a partially inverse spinel structure in which majority of the A (tetrahedral) site was occupied by Fe^{3+} [18, 19]. In this work, the Fe^{3+} in cobalt ferrite catalyst composed three components: A site (sextet), B (octahedral) site (sextet with broad peaks reflecting binomial distribution of cobalt atoms at the A site) and the smallest particles with superparamagnetic nature (quadrupole doublet). A less intense Fe^{3+} doublet component, accounting for less than 1% of the spectral area, may also be present in the spectra. Its contribution was smaller in the case of CFA-600, suggesting that higher calcination temperature tended to diminish its presence.

The spectra of samples CFN-500 and CFN-600 (Figure 4c, d) indicated the presence of the bcc $\text{Fe}_x\text{Co}_{1-x}$ alloy phase with an Fe:Co ratio close to 2:1, the fit of which was similar with the previous discussions [20]. A heavily broadened spectral component in CFN-500 was associated with the smallest Co-Fe alloy particles, which disappeared from the spectrum of CFN-600, in agreement with its larger characteristic particle size. A paramagnetic Fe^{3+} doublet component with a considerably smaller relative spectral area for CFN-600 (~2%) than for CFN-500 (~7%), suggested that this amount could be reduced by increasing the calcination temperature.

For the sample calcined under NH_3 atmosphere at 500 °C, both magnetic sextet and paramagnetic doublet can be detected (Figure 4e), indicating the coexistence of Co-Fe alloys and nitrides. In contrast, by increasing the calcination temperature to 600 °C, only one paramagnetic doublet can be observed (Figure 4f), whose Mössbauer parameters were consistent with that of Fe_2N [21]. It was concluded that pure nitrides were obtained at 600 °C.

With the assistance of Mössbauer spectroscopy, all the fine structures of the prepared Co/Fe-based catalysts were distinguished more detailed, which would be crucial to their further application.

2.3 Mechanism study and stability characterization

For the sake of comparing the properties of different kinds of cobalt-iron catalysts, pure cobalt-iron oxides, alloys, and nitrides which were obtained at 600 °C under different

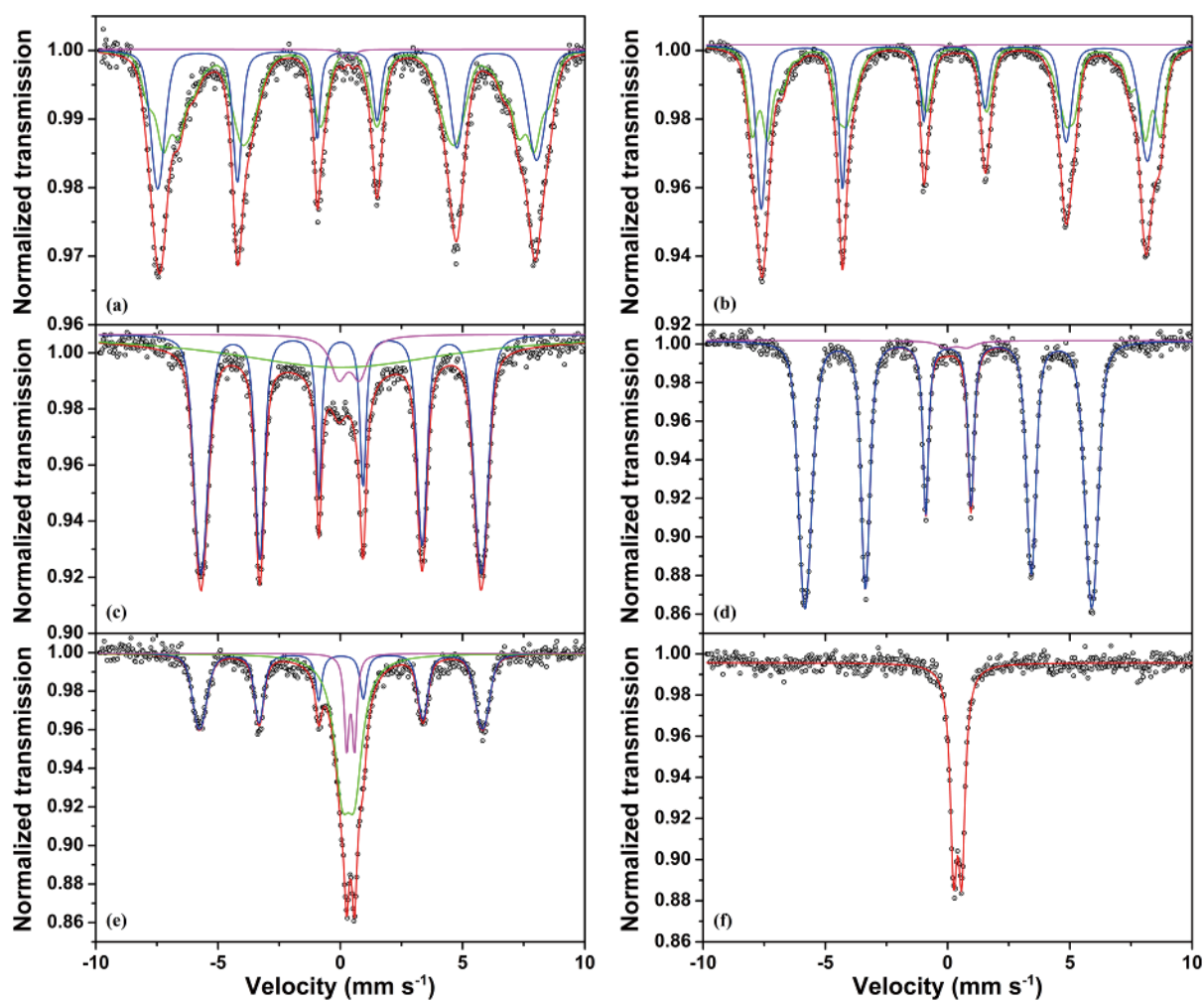


Figure 4. ^{57}Fe Mössbauer spectra of different cobalt-iron catalysts (a) CFA-500; (b) CFA-600; (c) CFN-500; (d) CFN-600; (e) CFNH-500, and (f) CFNH-600.

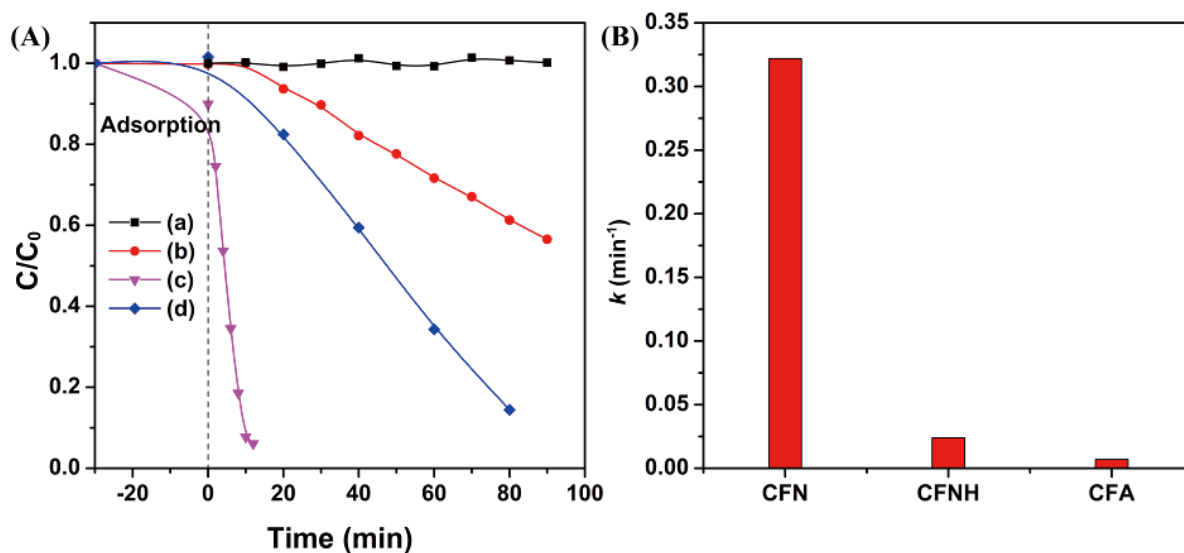
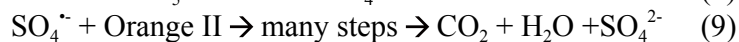
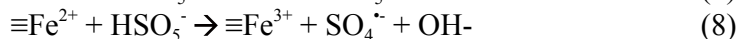
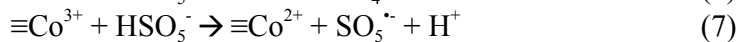
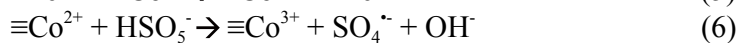
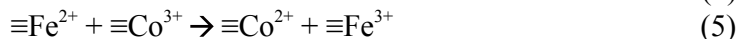


Figure 5. The Orange II degradation curves (A) and reaction rate constants k (B) calculated from $\ln(C_0/C)$ versus time of different catalysts through PMS activation (a) blank, (b) CFA-600, (c) CFN-600, (d) CFNH-600. (Conditions: Orange II, 50 mg L^{-1} ; Catalysts, 0.1 g L^{-1} ; Oxone, 0.5 g L^{-1} ; $T=22\pm 1 \text{ }^\circ\text{C}$)

atmospheres, were chosen for evaluation in the field of PMS catalytic activation for organic pollutants degradation, shown in **Figure 5**. The activity followed the sequences of CFN-600 > CFNH-600 > CFA-600, i.e. alloy > nitride > oxide.

In order to speculate the reaction mechanism, Mössbauer spectra were conducted to characterize the variation in the state of iron, combined with the XPS results. For the used CFA-600, there was no appreciable change in the valent of Fe³⁺ in the spinel, but the relative area of the paramagnetic Fe³⁺ doublet increased up to ~2.5% (**Figure 6a**). Co-Fe alloy was proved to be the most efficient in Orange II degradation, which may be due to its better reduction ability. According to the Mössbauer spectra and parameters (**Figure 6b**), the amounts of paramagnetic Fe³⁺ increased from ~2% to 9%, with a corresponding decrease of zero valent iron in Co-Fe alloy phase after reaction, indicating the participation of Fe⁰ as active sites resulting in the generation of oxidized Fe³⁺. No significant variation took place in the state of Fe in CFNH-600 (**Figure 6c**), suggesting the good stability of the catalysts, which was essential to their application in environmental remediation.

In consideration of other characterization techniques and literatures, mechanisms were proposed on the different Co/Fe-based catalysts. Taken Co-Fe alloy as an example, the following equations (1~9) can be considered.



3. Rational design of yolk/shell protective cobalt ferrite@mSiO₂ nanocomposites

3.1 Materials design and synthesis

Synthesis of the yolk/shell cobalt ferrite@mSiO₂ contained several steps, including RF spheres formation, metal loading, silica coating and templates removal, which were schematically illustrated in **Figure 7**. Firstly, the sacrificial templates of resorcinol formaldehyde (RF) spheres were prepared by extended Stöber method [22]. Then,

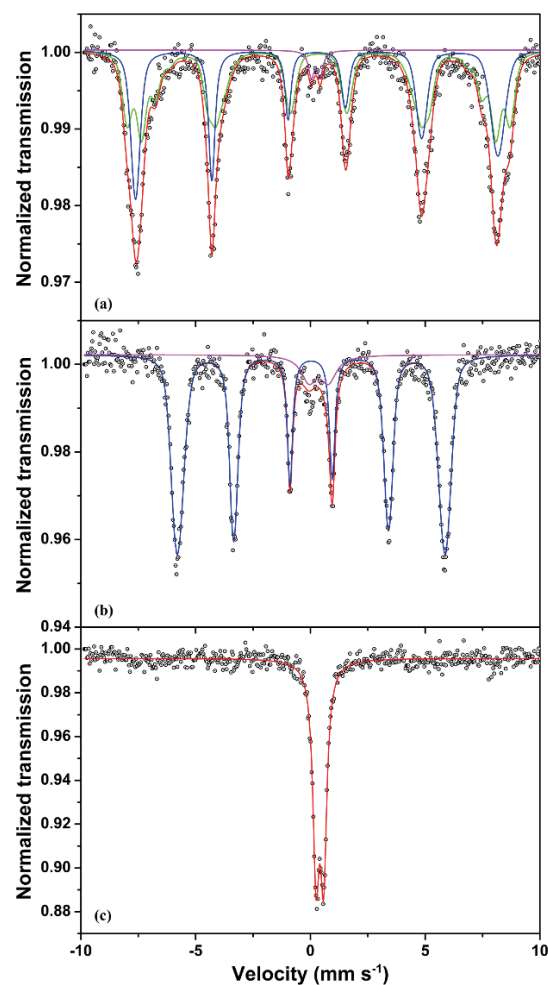


Figure 6. ⁵⁷Fe Mössbauer spectra of the used (a) CFA-600, (b) CFN-600, and (c) CFNH-600.

appropriate amount of Co(acac)₂ and Fe(acac)₃ (with Co:Fe molar ratio at 1:2) dissolving in ethanol were added into the above-mentioned mixture. The metal-doped RF spheres were collected by centrifugation and washed with water and ethanol for several times. For mSiO₂ coating, the Co, Fe-codoped RF spheres were redispersed in water-ethanol solution containing certain amounts of cetyltrimethyl ammonium bromide (CTAB), followed by the addition of ammonia and tetraethyl

orthosilicate (TEOS). With the help of CTAB, the Co, Fe-codoped RF spheres were readily coated by silica and the existence of CTAB also contributed to the formation of mesopores of silica shell. The final yolk/shell architecture was obtained by calcining the intermediate product of CoFe-RF@mSiO₂ to remove the templates and the organic species

from metal precursors, while at the same time, obtain the partially inverse spinel type cobalt ferrite, which was proved by powerful Mössbauer technique. Hereafter, the yolk/shell nanostructured catalysts were denoted as CFS-*n*, where *n* represents the amount (mmol) of iron precursor. The cobalt ferrite@mSiO₂ refers to CFS-0.3 if it is not specially labelled.

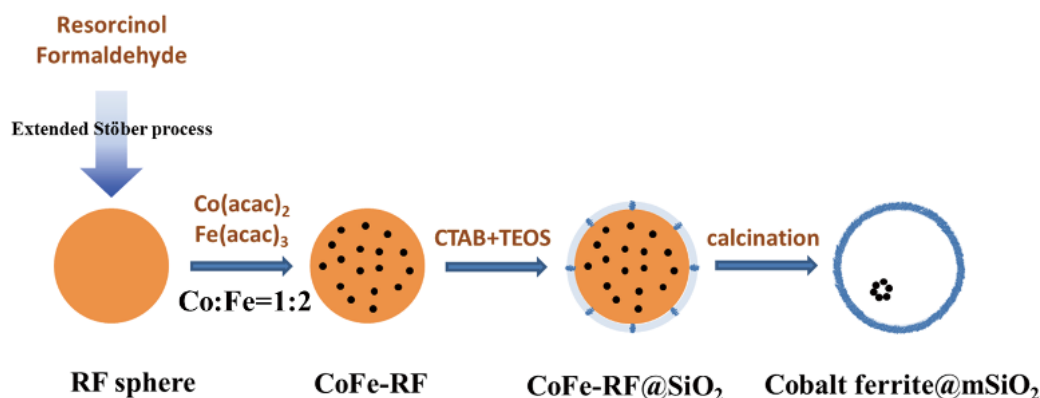


Figure 7. Schematic illustration of the preparation for the yolk/shell cobalt ferrite@mSiO₂ catalysts.

For comparison, the mSiO₂ supported cobalt ferrite catalyst was prepared through a conventional impregnation method. The mSiO₂ support was synthesized in basic mixed solvent system according to the reported method [23]. Then, corresponding amounts of cobalt and ferric precursors dissolved in ethanol were mixed with the prepared mSiO₂ spheres, under stirring homogeneously. The products were obtained after dry and calcination processes.

3.2 Mössbauer characterization

⁵⁷Fe Mössbauer spectroscopy was employed to ascertain the spinel structure of Fe-containing phase verified by XRD patterns in the yolk/shell nanostructured catalysts, as shown in **Figure 8**. The Mössbauer parameters resulting from the spectral fitting were listed in **Table 1**. As previously stated, CoFe₂O₄ tended to form with a partially inverse spinel structure. The overall cation can be expressed as (Co_{*x*}Fe_{1-*x*})[Co_{1-*x*}Fe_{1+*x*}]O₄ where the element symbols enclosed in parenthesis referred to cations (Fe³⁺, Co²⁺) situated at the A sites and square brackets referred to those of B sites. Given that CoFe₂O₄ was ferrimagnetic at RT, A-site and B-site Fe³⁺ ions were each expected to contribute to the ⁵⁷Fe Mössbauer spectrum of CoFe₂O₄ with sextet components reflecting magnetic splitting of the excited and ground

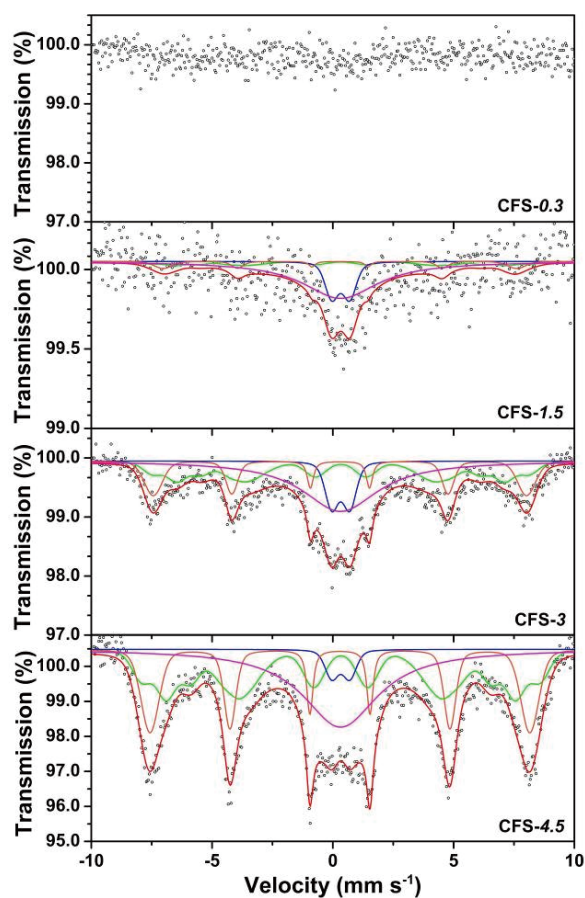


Figure 8. RT ⁵⁷Fe Mössbauer spectra of the prepared cobalt ferrite@mSiO₂

state nuclear levels of corresponding ^{57}Fe nuclei [24, 25].

In the RT Mössbauer spectra of the yolk/shell samples, the quadrupole doublet component with parameters of $\delta = 0.33(2)$ mm s $^{-1}$ and $\Delta = 0.73(2)$ mm s $^{-1}$ (referred to as “superparamagnetic (SP) doublet”) (**Table 1**) was consistent with corresponding values ($\delta \approx 0.35$ mm s $^{-1}$, $\Delta \approx 0.76$ mm s $^{-1}$) obtained for SP CoFe_2O_4 particles with a crystallite size of ~ 6 nm [26]. Considering the morphologies from TEM images, it was plausible to ascribe this doublet to the smallest spinel nanoparticles situated inside the mSiO_2 (Figure **8b-d**). The broad spectrum with dominant contribution to the spectral area in the velocity range of -2 to $+2$ mm s $^{-1}$, which was approximated with a broad Lorentzian singlet component (referred to as “SP singlet”), might originate from somewhat larger particles for which the frequency of SP relaxation was slower. The sextet components should then originate from the relatively larger particles situated mainly outside the cavities of the yolk/shell architectures. In order to account for the observed spectral features, the previously reported model was adopted [27-29]. The magnetic sextet spectral components were fitted with B-site Fe^{3+} ions by assuming a binomial distribution of Co^{2+} ions at the n.n. A-sites. In the fit, the effects of n.n. A-site Co^{2+} ions on the magnitude of the corresponding $B_{\text{hf,B}}$ value were assumed to be equal, additive and independent of their configuration, such that $B_{\text{hf,B}}$ depends exclusively on the number of n.n. A-site Co^{2+} ions. The contribution of B-site Fe^{3+} ions to the observed Mössbauer spectra contained seven different sextet components with equal isomer shifts, suitably constrained relative area fractions, and hyperfine magnetic field values [30]. The relatively narrow hyperfine magnetic field distribution present in the sextet associated with A-site Fe^{3+} ions was taken into account as a Gaussian shaped hyperfine magnetic field distribution fitted in the form of a Voigt-based fitting (VBF) sextet component [30, 31].

In order to obtain well defined values for the physical parameters despite the moderate S/N (signal/noise) ratio of the obtained spectra (**Figure 8**), a simultaneous fit of the Mössbauer spectra of the samples CFS-4.5, CFS-3 and CFS-1.5 were conducted, where all these samples were assumed to show the same degree of inversion, i.e. the same x concentration of Co^{2+} ions at the A-sites. Thus,

$x = 0.205(7)$ was obtained which confirmed the partially inverse nature of the spinel, and the atomic distribution of $(\text{Co}_{0.21}\text{Fe}_{0.79})[\text{Co}_{0.79}\text{Fe}_{1.21}]\text{O}_4$, in excellent consistent with earlier observations [24, 25, 27, 28]. Hyperfine magnetic field values of A-site and B-site Fe^{3+} ions turned out to be smaller in CFS-3 than in CFS-4.5, in accordance with the TEM results, which indicated that collective magnetic excitations played a role in the reduction of hyperfine magnetic fields. The relative area fraction of SP doublet and singlet components increased in the order of CFS-4.5 $\rightarrow$ CFS-3 $\rightarrow$ CFS-1.5, also suggesting that a lower amounts of metallic precursors led to a higher fraction of the smallest SP particles in the final cobalt ferrite@ mSiO_2 nanostructured catalysts. The Fe isomer shift of these components were close to those of the magnetic sextets (**Table 1**), corroborating that the smallest particles possessed an atomic composition that was similar to that of larger ones.

3.3 Activity and recyclability comparison

The yolk/shell nanostructured catalysts were used as PMS activator for organic dyes degradation through SR-AOPs. **Figure 9(A)** displays the catalytic performances of different catalysts for Orange II degradation. In the case of the yolk/shell and supported catalysts adsorption experiments, as well as PMS alone and mSiO_2 /PMS system, no significant removal took place in the amount of Orange II during the tested 60 min. However, with the involvement of both catalysts and PMS, Orange II was degraded effectively. More than 90% Orange II was removed on cobalt ferrite@ mSiO_2 within 35 min, which was more efficient than the supported one with similar active metal contents (Co:1.11 wt%, Fe: 1.91 wt%) and the naked cobalt ferrite without mSiO_2 shells with higher metal content (about five-fold). The superior activity of yolk/shell catalyst was proposed to be resulted from the smaller size of the active spinel particles and the yolk/shell architecture characteristics, indicating the superiority and rosy prospect of yolk/shell architecture in SR-AOPs.

The recycle test results of the yolk/shell and supported catalysts in **Figure 9(B)** showed that the activity declined on both of the catalysts after five cycles, however, the yolk/shell one kept slower rate of descent than the conventional supported one. Surprisingly, the activities of the two catalysts were recovered to a great extent by a simple calcination

Table 1. ^{57}Fe Mössbauer parameters of the prepared yolk/shell samples, obtained from a simultaneous fit of the spectra of the indicated three samples with the assumption of a powder geometry without texture. Except the relative abundance and the hyperfine magnetic field parameters, corresponding fit parameter values were assumed to be the same in each of the three spectra. With the exception of the “SP singlet” component, all spectral components were assumed to be characterized by the same Lorentzian FWHM width parameter W_L . Numbers in parentheses denote the statistical uncertainty (1σ) of the last digit(s).

Parameters	CFS-4.5	CFS-3	CFS-1.5
Fe ³⁺ (B, octahedral)			
Model	7 sextet components with weights calculated according to a binomial distribution of Co atoms at the nearest neighbor tetrahedral sites, assuming that the hyperfine magnetic field sensed by the Fe ³⁺ nuclei at octahedral sites depends linearly on the number of Co atoms at n.n. tetrahedral sites.		
Relative abundance (%)	38.4(8)	29.9(9)	13(3)
δ (mm s ⁻¹)	0.33(2)		
B _{hf,0} (T)	51.2(2)	48.5(4)	49(4)
ΔB _{hf} (T)	−6.3(2)		
c(Co _A) (≡ x in (Co _x Fe _{1-x})[Co _{1-x} Fe _{1+x}]O ₄)	0.205(7)		
W _G (mm s ⁻¹)	0.81(5)		
W _L (mm s ⁻¹)	0.26(2)		
Fe ³⁺ (A, tetrahedral)			
Model	1 VBF sextet component reflecting a Gaussian shaped hyperfine magnetic field distribution with a standard deviation of σ (B _{hf}).		
Relative abundance (%)	25.3(3)	19.7(4)	8.4(1.9)
δ (mm s ⁻¹)	0.293(5)		
B _{hf} (T)	48.9(1)	48.0(1)	45.5(1.4)
σ (B _{hf}) (T)	1.95(9)		
W _L (mm s ⁻¹)	0.26(2)		
Fe ³⁺ (SP doublet)			
Model	1 doublet component composed of Voigt-shaped peaks.		
Relative abundance (%)	3.4(7)	10.4(1.0)	17.2(3.1)
δ (mm s ⁻¹)	0.33(2)		
Δ (mm s ⁻¹)	0.73(2)		
W _G (mm s ⁻¹)	0.51(5)		
W _L (mm s ⁻¹)	0.26(2)		
Fe ³⁺ (SP singlet)			
Model	1 Lorentzian singlet with large FWHM width accounting formally for a magnetic phase displaying superparamagnetic relaxation.		
Relative abundance (%)	33(1)	40(2)	62(7)
δ (mm s ⁻¹)	0.32(3)		
W _L (mm s ⁻¹)	3.8(3)		

δ - ^{57}Fe isomer shift relative to α -Fe at room temperature, Δ - quadrupole splitting, W_L - Lorentzian FWHM width of absorption peaks, W_G - Gaussian FWHM width of Voigt-shaped absorption peaks, $B_{\text{hf},0}$ - hyperfine magnetic field sensed by Fe^{3+} nuclei at octahedral sites with no Co atom at nearest neighbor (n.n.) tetrahedral sites, ΔB_{hf} - change in the hyperfine magnetic field sensed by Fe^{3+} nuclei at octahedral sites when the number of Co atoms at n.n. tetrahedral sites increases by one, $c(\text{Co}_A)$ - concentration of Co atoms at tetrahedral sites, B_{hf} - mean value of the hyperfine magnetic field sensed by Fe^{3+} nuclei at tetrahedral sites, σ (B_{hf}) - standard deviation of the Gaussian shaped distribution in the B_{hf} values.

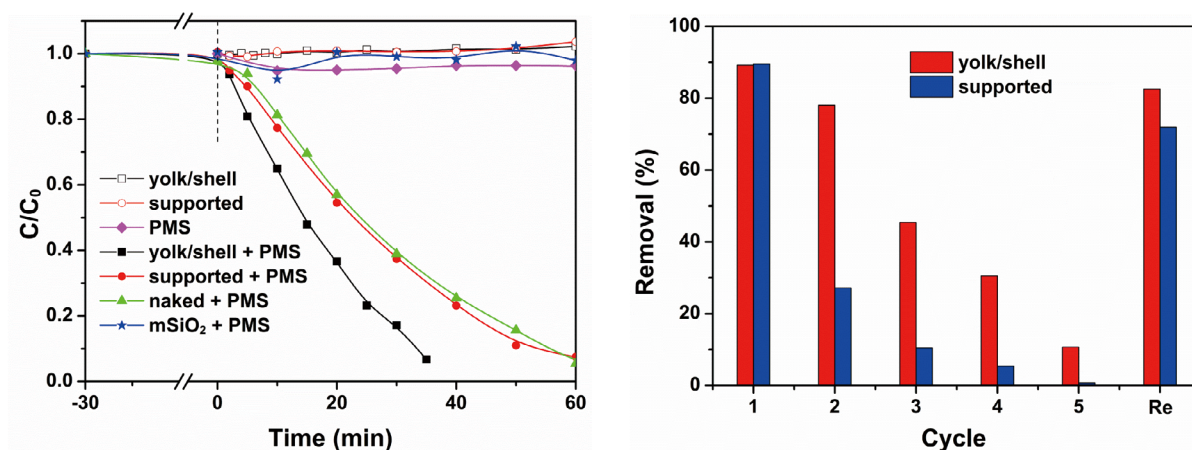


Figure 9. Activity (A) and reusability (B) comparison among yolk/shell architected cobalt ferrite @ mSiO₂ and the conventional supported and naked ones in PMS catalytic activation for Orange II degradation. (Conditions: [Orange II]₀ = 20 mg L⁻¹, [catalyst]₀ = 0.2 g L⁻¹, [Oxone]₀ = 1 g L⁻¹, T = 30 °C, naked cobalt ferrite (0.05 g L⁻¹), t(yolk/shell) = 35 min, t(supported) = 60 min.)

treatment at 400 °C in air, especially for the yolk/shell one, whose activity was recovered to almost the same level as the original one. Such phenomenon manifested that the adsorption of the intermediate organic species generated on active sites might be the major factor to the deactivation of the catalysts. Both the activity and stability were proved to be superior to the supported one, indicating the advantages of the yolk/shell catalyst in PMS activation for organics degradation.

Conclusions and Prospects

A series of iron-based catalysts were synthesized by different strategies and applied in the field of PMS activation for organic pollutants degradation. Mössbauer spectroscopy played an important role in the structure determination and mechanisms study. In these works, the performances were gradually optimized and improved by structure and morphology design. However, further studies were still needed to improve the activity and stability of PMS activation catalysts, for example, active carbon-introducing, N-doping, S-doping, and so on. The advantages of environmental friendly, abundant, low price, and easy to recover through magnetic separation made the iron-based catalysts be promising in the field of environmental remediation.

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