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A Co–Fe Prussian blue analogue for efficient Fenton-like catalysis: the effect of high-spin cobalt

Co–Fe PBA exhibits excellent Fenton-like performance for the degradation of BPA. The largely elongated  $SO_4$ –OH bond length and facilitated electron transfer over the high-spin Co<sup>II</sup> sites are the main factors for the efficient PMS activation.





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## A Co–Fe Prussian blue analogue for efficient Fenton-like catalysis: the effect of high-spin cobalt<sup>†</sup>

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Herein, we, for the first time, report a high spin Co–Fe Prussian blue analogue (Co–Fe PBA) as a highly efficient Fenton-like catalyst for sulfate radical (SO<sub>4</sub><sup>•-</sup>) production. Our experiments and density functional theory (DFT) calculations show that the largely elongated SO<sub>4</sub>–OH bond length, strengthened adsorption and facilitated electron transfer for peroxymonosulfate (PMS) activation catalyzed by high-spin (HS) Co<sup>II</sup> are the main factors contributing to its excellent activity.

Hydroxyl radicals (HO•), generated from the Fenton or Fentonlike process, are applied to degrade various organic compounds.<sup>1,2</sup> However, the traditional Fenton process requires acidic pH conditions and has relatively low efficiency.<sup>3</sup> In recent years, the  $SO_4^{\bullet-}$  based Fenton process has gradually attracted widespread attention due to its high oxidation potential and mild pH requirements.<sup>4</sup> Among all the catalysts that can activate PMS  $(HSO_5^-)$  to produce active  $SO_4^{\bullet-}$ , a cobalt-based nanomaterial was considered as an optimum activator.<sup>5</sup> However, there has been no report on the effect of different spin states of the cobalt on the sulfate radical-mediated Fenton-like activity.

Prussian blue analogues (PBAs) are a class of metal–organicframework (MOF) structures constructed from octahedral  $[M_1(CN)_6]^{n-}$  anionic groups and  $M_2^{n+}$  ions. The different coordination modes of the dual metals, with high spin (HS)  $M_1$  coordinated to N and low spin (LS)  $M_2$  coordinated to C,<sup>6</sup> make PBAs ideal models for studying the effect of the spin state of Co on catalytic PMS activation. Our group has reported the excellent Fenton

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activity and the efficient sorption of cesium by Fe–Co PBA.<sup>7–9</sup> But the effect of the different spin states of the cobalt on the sulfate radical-mediated Fenton-like activity has not been investigated.

In this work, we systematically investigate the Fenton-like performance of M–Fe PBAs (M = Co, Cu, Fe, Ni), Fe–Co PBA, Co–Co PBA and  $K_3[Co(CN)_6]$  for PMS activation. Among them, Co–Fe PBA exhibits the highest efficiency for the production of sulfate radicals for the degradation of bisphenol A (BPA). Moreover, experiments and density functional theory (DFT) calculations show that the largely elongated SO<sub>4</sub>–OH bond length, strengthened adsorption energy and facilitated electron transfer for PMS activation catalyzed by N-coordinated high-spin Co<sup>II</sup> are the main factors contributing to its excellent activity.

Fig. 1a shows the heterogeneous dominated Fenton-like activity of Co–Fe PBA (Fig. S1, ESI†) compared to several other M–Fe PBAs (M = Cu, Ni, Fe), Fe–Co PBA, Co–Co PBA, and  $K_3$ [Co(CN)<sub>6</sub>] with similar morphologies (Fig. S2, ESI†). Co–Fe PBA exhibited excellent Fenton-like performance with good stability (Fig. S3–S5, ESI†) as compared with recently reported results (Table S1, ESI†), and the removal efficiency of BPA reached 93% in 30 min under our experimental conditions. The BPA degradation efficiencies of Ni–Fe, Fe–Fe and Cu–Fe PBA in 30 min were only 3%, 7% and 12%, respectively, under the same experimental conditions. The degradation of BPA by Co–Fe PBA obeyed pseudo-first order kinetics  $\ln(C_0/C_t) = kt$ 



**Fig. 1** Fenton-like activities (a) and rate constants (b) of M–Fe PBAs (M = Co, Cu, Ni, Fe), Fe–Co PBA, Co–Co PBA and K<sub>3</sub>[Co(CN)<sub>6</sub>]. Reaction conditions: [BPA] = 20 mg L<sup>-1</sup>, [PMS] = 0.1 g L<sup>-1</sup>, catalyst = 0.1 g L<sup>-1</sup>, T = 308 K, initial solution pH = 6.0.



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(Fig. S6, ESI<sup>†</sup>), and the relevant rate constants of the different reaction systems are shown in Fig. 1b. The above results clearly indicate that a cobalt-based Co–Fe PBA MOF material is an optimum activator of PMS.

To study the effect of the spin state of cobalt on the Fentonlike reaction, we compared the Fenton-like properties of Co(HS)– Co(LS) and Fe–Co(LS) PBAs (Fig. 1a). Under the same experimental conditions, the BPA degradation efficiency of Co(HS)–Co(LS) was 93% in 30 min, while that of Fe–Co(LS) PBA was only 48% in 30 min. Besides, the normalized Fenton-like activity of Co(HS)– Co(LS) PBA ( $1 \times 10^{-4} \text{ min}^{-1} \text{ g m}^{-2}$ ) was also higher than that of Fe–Co(LS) PBA ( $3 \times 10^{-5} \text{ min}^{-1} \text{ g m}^{-2}$ ) (Fig. S7 and Table S2, ESI†), which clearly indicates that the high-spin cobalt in Co(HS)– Co(LS) PBA has excellent Fenton-like activity. Moreover, the Fenton-like activities of Co(HS)–Co(LS) PBA and Co(HS)–Fe PBA are similar, and K<sub>3</sub>[Co(LS)(CN)<sub>6</sub>] shows low Fenton-like performance, which indicates that the low-spin cobalt contributes little to the good Fenton-like activity. The above results demonstrate the important role of high spin Co.

<sup>57</sup>Fe Mössbauer spectroscopy was applied to confirm the oxidation state and the spin state of the iron ions of PBAs (Fig. 2a and Fig. S8, Table S3, ESI†).<sup>10,11</sup> The obtained Mössbauer isomer shifts of  $K_3$ [Fe(CN)<sub>6</sub>] (Fe–C) and M–Fe PBAs (M = Co, Cu, Ni) (M–N–C–Fe) indicate that the Fe species coordinated to C are low-spin Fe, and the obtained Mössbauer isomer shifts of Fe–Co PBA (Fe–N–C–Co) show that the Fe species coordinated to N are high-spin Fe. The two kinds of Fe species of Fe–Fe PBA (Fe–N–C–Fe) (*i.e.* Prussian blue) could be separately assigned to low-spin Fe coordinated to C and high-spin Fe coordinated to N. Therefore, we can reasonably infer that the Co species coordinated to N are high-spin Co in Co–Fe PBA (Co–N–C–Fe) and Co–Co PBA (Co–N–C–Co), and the Co species coordinated to C are low-spin Co in Fe–Co PBA (Fe–N–C–Co), Co–Co PBA (Co–N–C–Co) and  $K_3$ [Co(CN)<sub>6</sub>] (Co–C), which were confirmed by magnetization measurements (Fig. S9, ESI†).

The X-ray photoelectron spectroscopy (XPS) of Co-Fe PBA before and after the reaction was performed to explore the

ntensity (a.u.

788 786

(b) Co 2 p<sub>3/2</sub> before reaction

Co 2 p<sub>3/2</sub> after reaction

784 782 Binding Energy (eV) 780



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activation mechanism of PMS. Fig. 2b shows the high resolution XPS results of Co 2p<sub>3/2</sub> on the Co-Fe PBA surface before and after the catalytic process. The peak with a binding energy of 781.4 eV could be assigned to Co<sup>II</sup>, the peak with a binding energy of 782.6 eV could be ascribed to Co<sup>III</sup>, and the peak at 784.8 eV could be assigned to the satellite peak of Co<sup>II,12,13</sup> The relative contributions of Co<sup>II</sup> decreased and that of Co<sup>III</sup> increased after the Fenton-like reaction, indicating that Co<sup>II</sup> is the active site in the Fenton-like reaction. Fig. S10 (ESI<sup>+</sup>) shows the high resolution XPS spectra of Fe  $2p_{3/2}$  on the Co-Fe PBA surface before and after the catalytic process. Two peaks with binding energies of 709.9 and 711.4 eV could be assigned to Fe<sup>III</sup>, and the peak with a binding energy of 708.2 eV could be assigned to Fe<sup>II</sup>.<sup>14,15</sup> The highresolution XPS results of Fe 2p<sub>3/2</sub> and the relative contributions of the peaks of Fe<sup>III</sup> and Fe<sup>II</sup> showed negligible changes before and after the reaction, implying that iron was not the active site of the Fenton-like reaction. The above results suggest that the oxidizing reaction occurred on the catalyst surface and the excellent Fenton-like activity of Co-Fe PBA mainly originated from Co<sup>II</sup> in its structure.

The involved radical intermediates were probed by radical scavenger experiments. When t-butanol (TBA) (0.2 M), an effective radical scavenger for HO<sup>•</sup>,<sup>16</sup> was added to the reaction solution, the degradation efficiency showed a slight decrease, suggesting minor contributions of HO<sup>•</sup> to the overall BPA oxidation. However, when methanol, a widely used radical scavenger for both  $SO_4^{\bullet-}$  and HO<sup>•</sup>,<sup>17</sup> was added to the reaction solution, more than 70% decrease of the BPA removal efficiency was observed (Fig. S11a, ESI<sup>+</sup>). The results suggest that the radical intermediates involved in the activation of PMS by Co-Fe PBA were SO4 •- and HO•, and the dominant reactive intermediate during the PMS activation by Co-Fe PBA was  $SO_4^{\bullet-}$ . To further confirm the identity of the involved reactive intermediates, electron spin resonance/5,5dimethyl-1-pyrroline-N-oxide (ESR/DMPO) experiments were carried out. As shown in Fig. S11b (ESI<sup>+</sup>), no peaks were identified when the BPA + DMPO system was tested, indicating that no radicals could be produced without PMS. However, when the BPA + PMS + DMPO system was tested, characteristic signals for DMPO-<sup>•</sup>OH adducts (with  $\alpha_N = \alpha_H = 14.9$  G) were observed,<sup>18</sup> suggesting the production of hydroxyl radicals by the strong hydrolytic process of  $HSO_5^-$  as shown in eqn (1) and (2).<sup>19</sup> When Co-Fe PBA was added into the BPA + PMS + DMPO system, the observed characteristic signals of DMPO-OH adducts and DMPO-SO<sub>4</sub><sup>•-</sup> adducts (with  $\alpha_N = 13.2$  G and  $\alpha_H =$ 9.6 G) reveal that both  $SO_4^{\bullet-}$  and HO<sup>•</sup> were generated during the activation of PMS by Co-Fe PBA.<sup>20</sup>

$$HSO_5^{-} + H_2O \leftrightarrow H_2O_2 + HSO_4^{-}$$
(1)

$$H_2O_2 \rightarrow HO^{\bullet} + HO^{\bullet}$$
 (2)

Therefore, the overall activation mechanism of PMS over Co–Fe PBA could be proposed as follows (eqn (3)–(5)). Firstly, the  $HSO_5^-$  species were adsorbed onto the surface of the catalyst and then activated by the high-spin Co<sup>II</sup> to produce  $SO_4^{\bullet-}$  radicals, as shown in eqn (3). At the same time, HO<sup>•</sup>

(a)

**Fransmission** (%)

Co-Fe PBA

Fe-Co PBA

-2 0 Velocity (mm s<sup>-1</sup>) radicals could also be produced through eqn (4). These involved radicals could degrade the BPA as shown in eqn (5).

$$\operatorname{Co}^{\text{II}}(\text{HS}) + \operatorname{HSO}_5^- \to \operatorname{Co}^{\text{III}}(\text{HS}) + \operatorname{SO}_4^{\bullet^-} + \operatorname{OH}^-$$
 (3)

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH$$
 (4)

$$SO_4^{\bullet^-/\bullet}OH + BPA \rightarrow \text{intermediates} + CO_2$$
 (5)

Theoretical calculations were carried out to investigate the intricate interactions between the PMS and PBAs. The favorite adsorption configurations of the PMS molecule adsorbed on the (200) surfaces of the different types of PBAs are shown in panel (a) of Fig. S12 and S13 (ESI<sup>+</sup>). Note that the (200) surface was considered in density functional theory (DFT) calculations based on X-ray diffraction (XRD) results (Fig. S14 (ESI<sup>+</sup>)) where the peak of the (200) facet is the highest for M-Fe PBAs. In addition, spin states were also set based on experimental results, i.e. for the different types of PBAs considered in the PBA type column in Table S4 (ESI<sup>+</sup>); the metals in the front have a high spin (HS) state, while the metals at the back have a low spin (LS) state. The experimental results above demonstrated that Co-Fe PBA shows the best performance for PMS activation compared with the other PBAs without the Co atom. As shown in Fig. S12B-Da (ESI<sup>†</sup>), it can be found that the PMS molecule in the most stable structures of the Cu-Fe, Fe-Fe and Ni-Fe PBA systems undergoes structural rearrangement after structure relaxation, where the H atom in the PMS molecule detaches from the hydroxyl group and binds with the O atom in the SO<sub>4</sub> group. This rearranged structure can't produce sulfate radicals  $(SO_4^{\bullet-})$  during the reaction process. On the other hand, the other adsorption configurations may also co-exist if a slight energy difference between the configurations is present. Therefore, the sub-stable structures of PMS on Co-Fe, Cu-Fe, Fe-Fe, and Ni-Fe PBAs are also shown in Fig. S12A-Db (ESI<sup>+</sup>), where PMS rearrangement occurs in the case of Co-Fe PBA, while the PMS structure remains in the cases of Cu-Fe and Fe-Fe, Ni-Fe PBAs. Note that the energy difference between the most stable and sub-stable configurations of each PBA is the difference in their corresponding PMS adsorption energies shown in Table S4 (ESI<sup>†</sup>). The corresponding calculation results are also summarized in Table S4 (ESI<sup> $\dagger$ </sup>).  $l_{O-O}$  is the O–O bond length of SO<sub>4</sub>–OH in PMS on PBAs after the geometry optimization and the  $l_{O-O}$  in isolated PMS molecule is 1.350 Å. Q is the electron transfer from PBA to PMS. It is observed from Table S4 (ESI<sup>+</sup>) that the adsorption of PMS on the most stable PBAs is quite strong in the range of chemical adsorption, which induces a relatively large charge transfer from PBA to PMS. This is also consistent with the adsorption configurations shown in Fig. S12 (ESI<sup>+</sup>), where chemical binding between PMS and PBA is found. In addition, the  $l_{O-O}$  of PMS without structural rearrangement in the most stable or sub-stable structure was remarkably prolonged compared with that of free PMS. All these illustrate that the adsorbed PMS molecule is activated and has a great tendency to generate sulfate radicals (SO<sub>4</sub> $^{\bullet-}$ ) and hydroxyl radicals ( $^{\bullet}$ OH). However, the adsorption of PMS on Co-Fe PBA is the strongest and a longer  $l_{O-O}$  is present compared with the other PBAs



**Fig. 3** The pathways of the free radical production process on the most stable Co–Fe PBA (a) and Co–Co PBA (b), where IS, TS and FS represent the initial structure, transition structure and final structure of the reaction, respectively.

without Co atoms, which demonstrates that Co–Fe PBA exhibits the best performance for PMS activation among all the investigated PBAs. On the other hand, the most stable structures of PMS on Cu–Fe, Fe–Fe and Ni–Fe PBAs can't generate  $SO_4^{\bullet-}$  due to the rearrangement of the PMS configuration. They also suggest that activation of PMS to generate  $SO_4^{\bullet-}$  by Cu–Fe, Fe–Fe and Ni–Fe PBAs was difficult due to the relatively big difference of  $E_{ads}$  between the most stable and sub-stable configurations or the low effect on the PMS activation, further confirming their poor performances for BPA degradation in the experiment.

In order to further understand the active site in PBA and the effect of spin states on the activation of PMS, the adsorption configurations of the PMS molecule adsorbed with different types of Co spin, including Co(HS)-Co(LS) PBA, Fe(HS)-Co(LS) PBA and the precursor K-Co(LS) along the (200) surfaces were also calculated and the corresponding structures are shown in Fig. S13 (ESI<sup>†</sup>). For the most stable configuration of the PMS molecule adsorbed in Co-Co PBA as shown in Fig. S13Aa (ESI<sup>+</sup>), the two oxygen atoms of PMS bonded with the Fe and Co atoms of the substrate, but no structural rearrangement occurred, which is similar to the stable structure of Co-Fe PBA discussed earlier. On the other hand, the sub-stable adsorption configurations of PMS on Co-Co PBA with the rearranged PMS structure and on Fe-Co PBA with the original PMS structure are shown in Fig. S13Ab (ESI<sup>†</sup>) and Fig. S13Bb (ESI<sup>†</sup>). For the most stable configuration of the PMS molecule adsorbed in the K-Co PBA precursor along the (200) surface as shown in Fig. S13C (ESI<sup>+</sup>), the PMS rearrangement occurred too. However, the sub-stable structure with unarranged PMS on K-Co PBA was not found. All the calculated results in terms of  $l_{O-O}$ , Q and  $E_{ads}$  of Co-PBAs are also listed in Table S4 (ESI†). It shows that the adsorption energies of PMS on the most and sub-most stable Co-Co and Fe-Co PBAs are quite strong and chemical adsorption occurs as confirmed by the chemical bonds between PMS and the PBAs in Fig. S13 (ESI<sup>†</sup>). The strong adsorption also induces a relatively large charge transfer from the PBA to PMS. Similar to Co-Fe PBA, the  $l_{O-O}$  of PMS in the most stable Co-Co PBA system obviously increased compared with that of free PMS, indicating its strong tendency to generate sulfate radicals  $(SO_4^{\bullet-})$  and hydroxyl radicals (•OH). The adsorption energy of PMS on the most stable K-Co PBA precursor indicates that weak physical adsorption occurs, with PMS dissociating into SO3 and O2H

groups as shown in Fig. S13C (ESI<sup>†</sup>). Although the adsorption energy of PMS on Co-Fe PBA is slightly lower than that on Fe-Co PBA for the most stable structure, PMS on Fe-Co PBA can't produce free radicals due to the PMS structural rearrangement. The adsorption results for the sub-stable configurations of both the Co-Co PBA and Fe-Co PBA systems are also shown in Table S4 (ESI<sup>†</sup>). It shows that PMS in the sub-stable configuration of Co-Co PBA rearranged, while the PMS structure remained in the sub-stable configuration of the Fe-Co PBA system. In addition, relatively big differences in  $E_{ads}$  are present between the most stable and sub-stable configurations for the two cases of Co-Co and Co-Fe PBAs, while the difference is relatively small for the Fe-Co PBA system. In other words, a sub-stable configuration of the Fe-Co PBA could coexist. However, the PMS is not so active due to its relatively short  $l_{0-0}$  compared with 1.466 Å and 1.456 Å in the most stable structures of the Co-Fe PBA and Co-Co PBA systems. Meanwhile, the most stable configuration of PMS on Fe-Co PBA can't produce free radicals due to the PMS structural rearrangement, which further proves that only the high-spin Co atoms are active sites for PMS activation. Therefore, the most stable adsorption configuration of PMS on PBA with high-spin cobalt (Co-Fe PBA or Co-Co PBA) exhibits almost the strongest adsorption energy and the longest  $l_{O-O}$  compared with the other PBAs with Co atoms, which demonstrates that the high spin state of the Co site shows the best performance for PMS activation, and thus the best performance for pollutant degradation, while the sub-stable configuration of Fe-Co PBA could also coexist and activate PMS weakly. This is consistent with the experimental results in Fig. 1.

To further confirm the effect of the high-spin state of cobalt on the activation of PMS, the reaction pathway of free radical production was calculated based on transition state theory as shown in Fig. 3. The energy barriers of the free radical production process on the most stable Co–Fe PBA and Co–Co PBA are 0.28 and 0.37 eV, respectively. The energy barriers of both reactions are less than the critical barrier of 0.91 eV.<sup>21</sup> Therefore, the PMS can be easily activated on Co–Fe and Co–Co PBAs. However, the reaction energy barrier in the case of Co–Fe PBA is a little lower than that in the case of Co–Co PBA, which indicates that the performance of Co–Fe PBA for PMS activation is better. This also agrees with the result of the longest  $l_{O-O}$  in Co–Fe PBA as shown in Table S4 (ESI†). More clear structural changes during the activation reaction of PMS on Co–Fe and Co–Co PBAs are shown in Fig. S15 (ESI†).

In conclusion, Co–Fe PBA exhibits excellent efficiency for the production of sulfate radicals for the degradation of BPA. Our experiments and DFT calculations show that the largely elongated  $SO_4$ –OH bond length, strengthened adsorption and facilitated electron transfer for PMS activation catalyzed by N-coordinated HS Co<sup>II</sup> are the main factors contributing to its excellent activity. This work was supported by the National Natural Science Foundation of China (21476232, 21607029 and 21777033), the International Partnership Program of Chinese Academy of Sciences (No. 121421KYSB20170020), the State Key Laboratory of Catalysis in the Dalian Institute of Chemical Physics (N-16-07), the Science and Technology Program of Guangdong Province (2017B020216003), the Science and Technology Program of Guangzhou City (201707010359), the National Supercomputing Centre in Guangzhou (NSCCGZ), the "1000 Plan" Program for Young Professionals of China, and the "100 Talents" Program of Guangdong University of Technology. This paper is dedicated to the 70th anniversary of the Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

#### Conflicts of interest

There are no conflicts to declare.

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