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Probing the Importance of Planar Surfaces and Crystal Edges for Electron Transfer within Iron-bearing Clays

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We demonstrated the importance of basal planes and crystal edge for electron transfer within montmorillonite (MK10) and nontronite (NAu-2) by a facile dye-sensitized photoreduction method. It was found that not all structural Fe in clay matrix are redox-active. The results are vital to utilization of naturally abundant clays in environmental redox chemistry.

Introduction

Fe-bearing clay minerals, with Fe contents varying from trace amounts to more than 30 wt% in nontronite, are ubiquitous in soils, aquatic sediments and sedimentary rocks.[1] The structural Fe^{2+}/Fe^{3+} redox couple at either octahedral or tetrahedral sites of clay lattice is an important redox buffer in subsurface environment that affects the cycling of other redox-active elements and nutrient, and contaminants transformation.[2-5] Numerous studies have confirmed that structural Fe^{3+} in a variety of Fe-bearing clays can act as a terminal electron acceptor for microbes.[6-9] Structural Fe^{2+} resulting from microbial or abiotic chemical reduction[10, 11], through complicated electron transfer reactions, is able to reduce a series of organic and inorganic pollutants, such as nitroaromatic[12], chlorinated solvents[13], heavy metals[14] and radionuclides.[15, 16]

Despite the biogeochemical significance of Fe redox chemistry in clay minerals, their electron transfer pathway remains unclear.[17] Since the structural Fe is usually embedded in an octahedral sheet sandwiched between two Si tetrahedral, the electron donors/acceptors are unlikely to physically contact with structural Fe species.[18] For an electron to be transported from aqueous electron donor to structural Fe^{3+}, it must diffuse or tunnel to the interior or bulk solid phase from the basal planes and/or crystal edge.[19] Recently a sophisticated Mössbauer spectroscopic study[17] has demonstrated that both basal planes and edge OH groups are the possible electron accepting sites for electron transfer from adsorbed Fe^{2+} to structural Fe in NAu-1 clay. However, it is still challenging to unambiguously identify the redox states of structural Fe in a dynamic electron transfer reactions.[17, 20] Also it remains unknown whether other Fe-bearing clays transfer electron in the similar way or have their own preferential electron accepting sites, depending on the diverse clay mineral properties (i.e. the total Fe content, Fe location environment and clay structure).

Here we investigated electron transfer to structural iron of typical dioctahedral smetites (i.e. montmorillonite and nontronite) by a facile photochemical reaction method, as recently developed by Zhao et al.[21-23] and our groups.[14, 24, 25] The excited dye is expected to donate electron to structural Fe. The generated structural Fe^{2+} can catalyze the H_2O_2 decomposition via a well-known Fenton reaction.[21] Hence, monitoring the decay kinetics of H_2O_2 is able to reflect the redox dynamics of structural Fe. To differentiate the electron accepting sites, two specific blocking compounds, polyphosphate for edge sites and benzyldimethyldodecylammonium bromide for siloxane basal planes, were used. The electron transfer processes were also investigated by fluorescence spectroscopy and X-ray photoelectron spectroscopy.

Experimental section

Chemicals. *N*, *N*-Diethyl-*p*-phenylenediamine (DPD) was from Sigma Chemical. Horseradish peroxidase (POD) was purchased from Huamei Biologic Engineering, China. Trisodium citrate, sodium bicarbonate, sodium dithionate, H_2O_2 (30%), potassium phosphate monobasic (KH_2PO_4), sodium phosphate monobasic (NaH_2PO_4), ethylenediaminetetraacetic acid (EDTA), sodium polyphosphate ($Na_5P_3O_{10}$), benzyldimethyldodecylammonium bromide (BDDAB), rhodamine B (RhB), rhodamine 6G (Rh6G), alizarine violet 3B (AV) and orange II (Org II) were of reagent grade and used without further purification. Barnstead UltraPure water (18.2 MΩ·cm) was used throughout the study.

Minerals. Montmorillonite K10 (MK10) was purchased from Aldrich, with cation exchange capacity (CEC) of 100 meq/100 g. The bulk samples of nontronite (NAu-2) were obtained from the Source Clays Repository of the Clay Minerals Society. Free iron oxides in the raw MK10 and NAu-2 were routinely removed with citrate/bicarbonate/dithionite (CBD) extraction. Briefly, 1 g MK10 was added to 50 mL solution of 0.3 M sodium citrate, 0.1 M sodium bicarbonate and 0.1 M sodium dithionate. Then the dispersion was shaken at 80°C. The obtained sample was treated with 2 M H_2O_2 at 80°C in order to reoxidize structural Fe(II) and remove organic impurities. The purified clays were dispersed in 1 M NaCl solution and stirred for 12 h to ensure the sufficient exchange of Na^+ and removal of carbonate. Then they were thoroughly washed with water and air dried. Inductively coupling plasma–Atomic emission spectra (ICP-AES) (JY-ULTIMA Co., Ltd, France) was used for measurement of iron in clays after HCl-HNO_3-HF digestion. The content of iron in purified MK10 and NAu-2 were determined to be 2.05% and 19.35%, respectively.

Procedure and analysis. A 500 W halogen lamp (Institute of Electric Light Source, Beijing) was used as the light source and fixed inside a cylindrical Pyrex jacket and cooled by circulating water. A cutoff filter was also positioned outside the Pyrex jacket to completely eliminate radiation below 450 nm to ensure irradiation of the dispersion only by visible light. The average light luminance was determined to be 6.5×10^4 lux by digital luminometer.

All the irradiation experiments were carried out in cylindrical Pyrex vessels (60 mL capacity, 3.8 cm diameter). The pH of the suspensions was adjusted to 7.0 ± 0.1 except otherwise notification. Usually 15 mg clay sample was added into 50 mL solution of 40 μM H_2O_2 and 20 μM dye. Prior to visible irradiation, each dye/clay suspension was stirred for at least 30 min in the dark to attain adsorption/desorption equilibrium. At a given time interval, about a 2 mL aliquot was sampled and centrifuged and immediately analyzed on a Hitachi U-3100 UV-Vis spectrophotometer. The residual concentration of H_2O_2 was determined spectrophotometrically at 551 nm by the DPD method.[26] For X-ray photoelectron spectroscopy (XPS) analyses, the specimens containing dye and clays were prepared by centrifuging the dye-containing dispersion and freeze-dried. XPS measurement of the samples was carried out on the 2201-XL multifunctional spectrometer (VG Scientific England) using Al Kα radiation.

Results and discussion

H_2O_2 decomposition catalyzed by structural Fe. The photoreduction of H_2O_2 was used to probe the electron transfer reaction occurring on basal planes or edge surface. RhB was selected considering the low redox potential of its excited states (-1.09 V vs NHE[27]) compared to that of structural Fe^{3+} (~0.44 V vs NHE[18]) and its high affinity to clay surface. MK10 and NAu-2 were compared because of their similarity in clay structure and difference in Fe loading. Isomorphic substitutions of Si^{4+} by Fe^{3+} generally lead to a negative charge of the layers[28], so RhB, a cationic dye (see its structure in ESI-Fig. 1), can be readily attracted toward the anionic layer. Over 94% of 20 μM of RhB was adsorbed onto the clay surfaces. To examine the electron transfer pathways from electron donor (excited dye) to acceptor (structural Fe), H_2O_2 decomposition in dye/clay systems was monitored. H_2O_2 was considerably stable under visible irradiation (>450 nm). Generally, the photoinduced charge separation between the dye and H_2O_2 occurs in a rather inefficient way in the homogeneous solution. Accordingly, most of the dyes are rather stable in the dilute H_2O_2 solution under visible light irradiation. However, in the presence of RhB and clays, a complete decomposition of H_2O_2 was observed within 180 min (Fig. 1a). No leaching of iron in the suspension was detected by spectrophotometric method, indicating a clay-mediated photochemical mechanism rather than a homogeneous Fenton reaction works in these systems. It is somewhat surprising that NAu-2 (~20 wt% Fe) and MK10 (~2 wt% Fe) with distinct Fe loading exhibited a similar H_2O_2 decomposition kinetics whenever RhB or other dyes were used (ESI-Fig. 2).

To differentiate the roles of basal planes and edge surface, two blocking compounds was used. Polyphosphate is known to specifically mask the edge surface[29], while BDDAB, a cationic surfactant, can intercalate into clay interlayer but cannot excited by visible light.[21] If excess polyphosphate and BDDAB are assumed to completely occupy the edge and basal interlayer, respectively, the adsorption of RhB was estimated as ~75% at basal plane and ~25% at edge surface for MK10, ~85% at basal plane and ~15% at edge surface for NAu-2. As polyphosphate was added to clay suspensions, the extent of H_2O_2 decomposition decreased by ~70% for NAu-2 within 180 min, but without measurable effect on MK10 system (Fig. 1a), implying the importance of edge site for NAu-2 electron transfer. In contrast, addition of BDDAB inhibited the decay of H_2O_2 by ~50% in MK10/dye system, but did not change the decomposition rate of H_2O_2 in NAu-2/dye solution (Fig. 1b). It indicates that basal plane may be very critical for MK10 to accept electrons. No exposed Fe^{3+} was present at basal interlayer or crystal surface since EDTA, a specific ligand for Fe^{3+}, did not lead to a notable change in H_2O_2 decomposition by MK10 and NAu-2 (Fig. 1c).

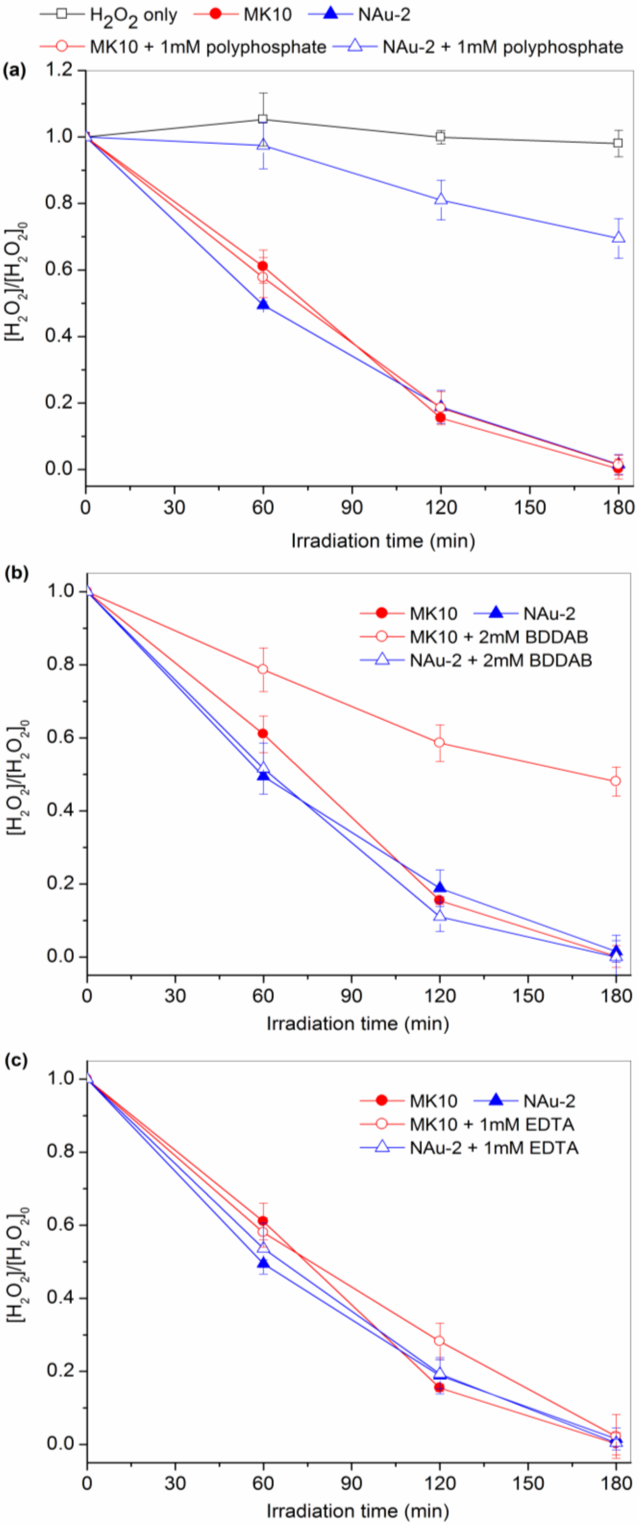

Fig. 1. Effect of (a) polyphosphate, (b) BDDAB and (c) EDTA on the photoreduction of H_2O_2 catalyzed by 0.3 g/L MK10 and NAu-2 in the presence of 20 μM RhB. H_2O_2, 40 μM; pH, 7.0.

Fluorescence quenching. The preference for electron accepting sites of MK10 and NAu-2 was further confirmed by fluorescence measurements. As shown in Fig. 2, mixing of RhB with polyphosphate or BDDAB had insignificant effect on the fluorescence of RhB. MK10 and NAu-2 at a concentration of 0.04 g/L effectively quenched the fluorescence of RhB at 576 nm, indicating an efficient electron transfer from the excited singlet state of dye to clays.[21] However, the presence of BDDAB and polyphosphate markedly inhibited the quenching of RhB fluorescence by ~95% for MK10 and ~42% for NAu-2, respectively. It provides further supporting evidence for the preference of electron transfer pathways of MK10 (from basal plane) and NAu-2 (from crystal edge). It should be noted that for each clay the sum of fluorescence intensity of clay/polyphosphate and clay/BDDAB was not equal to that of the original RhB solution. It is probably caused by the different fluorescence response of adsorbed dye with diverse structural configuration at basal surface and edge sites.[30]

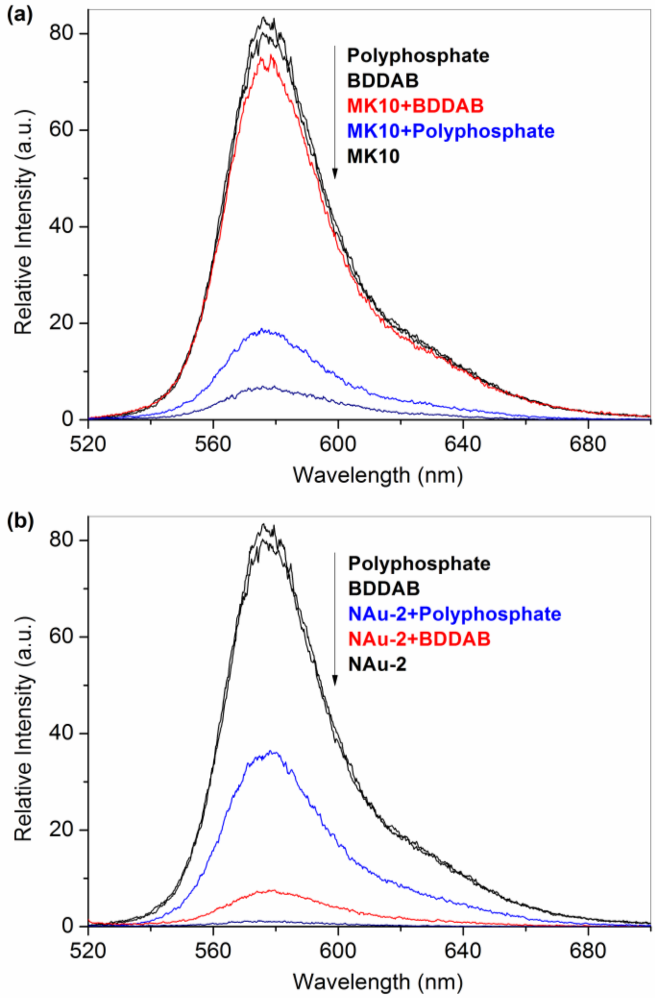

Fig. 2. Fluorescence quenching of RhB by (a) MK10 and (b) NAu-2. Excitation wavelength, 510 nm for RhB; slit: 2.5 nm. 0.04 g/L clays and 1 μM RhB were used in these fluorescence analyses. polyphosphate, 1 mM; BDDAB, 1 mM; pH, 7.0.

Importance of basal planes and crystal edge. Electron accepting sites in clay minerals might be basal oxygen within the silicate structure or Al^{3+} ions exposed at crystal edges.[31-33] With tetrahedral/octahedral substitution, the negative charge resides on the basal oxygens[28] which attract positively charged dye molecule. To investigate the interaction between positively charged $-N^+(Et)_2$ group of RhB and clays, the N 1s XPS of samples were measured (Fig.3). When RhB was adsorbed on NAu-2, only one N 1s peak centered at 399.5 eV was observed, similar to that of the pure RhB powder (399.4 eV).[34] In contrast, two N 1s peaks at 399.5 eV and 402.1 eV appeared in RhB/MK10 system. Wang et al.[34] reported a positive shift of 1.8 eV of N 1s binding energy of RhB on the fluoride-modified TiO_2 surface due to the strong interaction between F^- and $-N^+(Et)_2$ group of RhB. The large shift (2.6 eV) of N 1s peak should be attributed to the interaction between the basal oxygens and the $-N^+(Et)_2$ group of RhB. The strong chemical affinity of dye with basal oxygens may facilitate the electron transfer between excited dye and MK10, which can explain the predominance of basal planes in MK10 electron transfer as observed in H_2O_2 decay and fluorescence quenching experiments. Electrons can be transported over a distance of 3.2-3.3 Å, from basal plane oxygens to sandwiched structural Fe.[35]

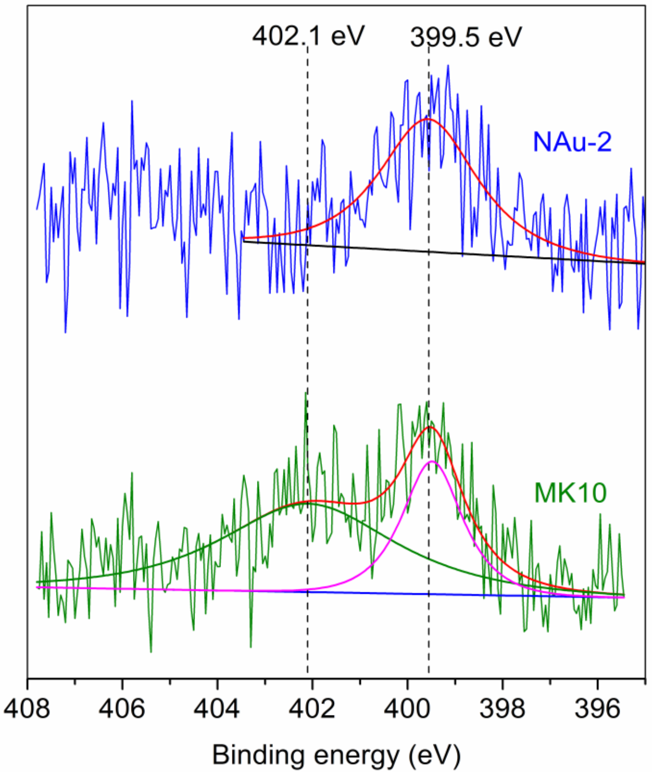

Fig.3. N 1s XPS spectra of RhB adsorbed on MK10 and NAu-2.

NAu-2 mineral may mainly use its edge surface as an electron accepting sites because treatment of NAu-2 with polyphosphate caused a marked decrease in H_2O_2 decay rate (Fig. 1a). Electrons may be transferred to the adjacent Fe(II)-O-Fe(III) pairs which would progress through the octahedral/tetrahedral sheet like a moving front.[36] Jaisi el al.[20] pointed out that Fe(III) in NAu-2 exists at *trans*, *cis* octahedral sites and tetrahedral sites. The tetrahedral Fe(III) accounts for 9% of total Fe(III) in NAu-2.[37] They reported that tetrahedral Fe(III) was the only bioreducible Fe(III) in the absence of an electron transfer facilitator. Similarly, Russell et al.[38] reported that nontronites containing tetrahedral Fe(III) such as NAu-2 were much more extensively reduced by chemical reductants like dithionite. Therefore, it is reasonable to presume that tetrahedral Fe(III) is the most active structural Fe toward H_2O_2 decomposition, in consistent with an early study on electrochemical reduction of H_2O_2 by SWa-1 clay.[39] They found that the active site for H_2O_2 reduction was iron on the tetrahedral edge surface of nontronite. If the tetrahedral Fe is responsible for the photoreduction of H_2O_2, it seems understandable that why NAu-2 and MK10 showed the similar reduction rate of H_2O_2, since the total tetrahedral Fe(III) (19.35 wt% × 9%=1.7 wt%) in NAu-2 was fairly close to the total Fe(III) (2.05 wt%) in MK10.

Conclusions

In this study, we developed a facile dye-sensitized photoreduction method to investigate the roles of basal planes and crystal edge of montmorillonite (MK10) and nontronite (NAu-2) in accepting electrons from excited dye, by monitoring the H_2O_2 decomposition catalyzed by structural Fe. Two specific blocking compounds to differentiate the electron accepting sites, polyphosphate for edge sites and benzyldimethyldodecylammonium bromide for siloxane basal planes, were used. It was found that significant electron transfer occurred from basal planes rather than edge surface for MK10 whereas crystal edge sites seem the most favorable locus for accepting electron to the interior of NAu-2. This conclusion was further confirmed by fluorescence quenching experiments. Only a small fraction of structural Fe in NAu-2 was redox-active and hence the rates of H_2O_2 decomposition by MK10 (total Fe, 2.05 wt%) and NAu-2 (total Fe, 19.35 wt%) were fairly close despite the wide difference in their Fe content. These findings inspire us to reassess the accessibility/availability of solid Fe pools in environmental redox reactions. The detailed electron transfer pathway from the sandwiched Fe(II) to the external electron acceptors such as H_2O_2 still remains unknown so far in this photosensitization process. Quantifying the respective contribution of basal planes and crystal edge to the overall efficiency of electron transfer, in a variety of clay/electron donors couples[17], deserves further investigations.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Chemical structure of RhB (ESI-Fig.1); Comparison of the photoreduction kinetics of H_2O_2 (ESI-Fig.2)]. See DOI: 10.1039/c000000x/

(1) J. W. Stucki. In *Iron in Soils and Clay Minerals*; J. W. Stucki, B. A. Goodman and U. Schwertmann, Eds.; D. Reidel: Dordrecht, The Netherlands, 1988; pp 625−675.

(2) J. E. Amonette. In *Electrochemical Properties of Clays*; A. Fitch, Ed.; CMS Workshop Lectures; The Clay Minerals Society: Aurora, CO, 2002; Vol.*10*, pp 89−146.

(3) M. Elsner, R. Schwarzenbach and S. B. Haderlein, *Environ. Sci. Technol*. 2003, **38**, 799.

(4) A. White, M. Peterson, *Geochim. Cosmochim. Acta* 1996, **60**, 3799.

(5) T. D. Jickells, Z. S. An, K. K. Andersen, A. R. Baker, G. Bergametti, N. Brooks, J. J. Cao, P. W. Boyd, R. A. Duce, K. A. Hunter, H. Kawahata, N. Kubilay, J. laRoche, P. S. Liss, N. Mahowald, J. M. Prospero, A. J. Ridgwell, I. Tegen and R. Torres, *Science* 2005, **308**, 67.

(6) J. W. Stucki, P. Komadel and H. T. Wilkinson, *Soil Sci. Soc. Am. J*. 1987, **51**, 1663.

(7) R. K. Kukkadapu, J. M. Zachara, J. K. Fredrickson, J. P. McKinley, D. W. Kennedy, S. C. Smith and H. Dong, *Geochim. Cosmochim. Acta* 2006, **70**, 3662.

(8) J. E. Kostka, E. Haefele, R. Viehweger and J. W. Stucki, *Environ. Sci. Technol*. 1999, **33**, 3127.

(9) H. Dong, D. P. Jaisi, J. Kim and G. Zhang, *Am. Mineral*. 2009, **94**, 1505.

(10) J. W. Stucki and C. B. Roth, *Soil Sci. Soc. Am. J*. 1977, **41**, 808.

(11) J. W. Stucki, D. C. Golden and C. B. Roth, *Clays Clay Miner*. 1984, **32**, 350.

(12) T. B. Hofstetter, A. Neumann and R. P. Schwarzenbach, *Environ. Sci. Technol*. 2006, **40**, 235.

(13) A. Neumann, T. B. Hofstetter, M. Skarpeli-Liati and R. P. Schwarzenbach, *Environ. Sci. Technol*. 2009, **43**, 4082.

(14) R.L. Liu, Y.G. Guo, Z.H. Wang and J.S. Liu, *Chemosphere* 2014, **95**, 643.

(15) J. Fredrickson, J. Zachara, D. Kennedy, R. Kukkadapu, J. McKinley, S. Heald, C. Liu and A. Plymale, *Geochim. Cosmochim. Acta* 2004, **68**, 3171.

(16) J. Yang, R. K. Kukkadapu, H. Dong, E. S. Shelobolina, J. Zhang and J. Kim, *Chem. Geol*. 2012, **291**, 206.

(17) A. Neumann, T. L. Olson and M. M. Scherer, *Environ. Sci. Technol*. 2013, **47**, 6969.

(18) C. Swearingen, J. Wu, J. Stucki and A. Fitch, *Environ. Sci. Technol*. 2004, **38**, 5598.

(19) L. B. Yan and G. W. Bailey, *J. Colloid Interface Sci*. 2001, **241**, 142.

(20) D. P. Jaisi, R. K. Kukkadapu, D. D. Eberl and H. L. Dong, *Geochim. Cosmochim. Acta* 2005, **69**, 5429.

(21) W.J. Song, M.M. Cheng, J.H. Ma, W.H. Ma, C.C. Chen and J.C. Zhao, *Environ. Sci. Technol*. 2006, **40**, 4782.

(22) M.M. Cheng, W.J. Song, W.H. Ma, C.C. Chen, J.C. Zhao, J. Lin and H.Y. Zhu, *Appl. Catal B: Environ*. 2008, **77**, 355.

(23) W.J. Song, J.H. Ma, W.H. Ma, C.C. Chen and J.C. Zhao, *J. Photochem. Photobiol. A: Chem.* 2006, **183**, 31.

(24) Z. Wang, W. Ma, C. Chen and J. Zhao, *J. Hazard. Mater.* 2009, **168**, 1246.

(25) R.L. Liu, D. X. Xiao, Y.G. Guo, Z.H. Wang and J.S. Liu, *RSC Adv*. 2014, **4**, 12958.

(26) H. Bander, V. Sturzenegger and J. Hoigne, *Water Res*. 1988, **22**, 1109.

(27) T. Takizawa, T. Watanabe and K. Honda, *J. Phys. Chem*. 1978, **82**, 1391.

(28) W. F. Bleam, *Clays Clay Miner*. 1990, **38**, 527.

(29) A. S. Michaels, *Ind. Eng. Chem*. 1958, **50**, 951.

(30) P. Čapková, P. Malý, M. Pospíšil, Z. Klika, H. Weissmannová and Z. Weiss, *J. Colloid Interf. Sci.* 2004, **277**, 128.

(31) D. H. Solomon, *Clays Clay Miner*. 1968, **16**, 31.

(32) Y. Soma and M. Soma, *Environ. Health Persp*. 1989, **83**, 205.

(33) B. K. G. Theng, *Clays Clay Miner*. 1971, **19**, 383.

(34) Q. Wang, C. Chen, D. Zhao, W. Ma and J. Zhao, *Langmuir* 2008, **24**, 7338.

(35) A. Meunier, Clays; Springer: Berlin, 2005; pp 1−60.

(36) P. Komadel, J. Madejova and J. W. Stucki, *Appl. Clay Sci*. 2006, **34**, 88.

(37) W. P. Gates, P. G. Slade, A. Manceau and B. Lanson, *Clays Clay Miner*. 2002, **50**, 223.

(38) J. D. Russell, B. A. Goodman and A. R. Fraser, *Clays Clay Miner*. 1979, **27**, 63.

(39) J.-M. Zen, S.-H. Jeng and H.-J.Chen, *J. Electroanal. Chem*. 1996, **408**, 157.

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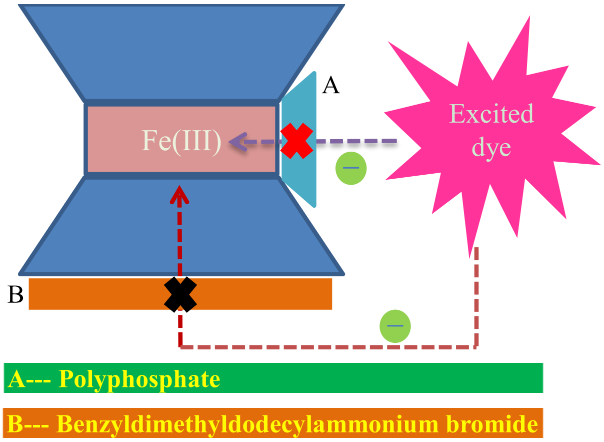

Text: clay with different binding environment of structural iron many differ in its mode of electron transfer from and to external electron donor/acceptor.