# Creation of a chain-like cationic iron species in montmorillonite as a highly active heterogeneous catalyst for alkane oxygenations using hydrogen peroxide

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A chain-like $Fe^{3+}$ species containing an Fe–O–Fe unit has been prepared within the interlayer space of a montmorillonite, which showed a very high catalytic activity (turnover frequency 386 h$^{-1}$ and turnover number 23 200) for the oxidation of cyclohexane with $H_2O_2$, affording cyclohexyl hydroperoxide as a major product.

Selective and efficient oxidation of alkanes using $O_2$ and $H_2O_2$ as oxidants is a challenging task in both industrial and academic fields. In relation to the alkane functionalisation chemistry on nonheme methane monoxygenase,[1] a diiron core is the key species in the oxidation of alkane C–H bonds.[2–4] A creation of solid materials involving the above diiron species is a promising strategy for designing bio-inspired heterogeneous catalysts for selective alkane oxidations.[5] Montmorillonites of smectite clays possess exchangeable cationic species between the negatively charged silicate layers, which have a potential ability to generate a unique structure of metal ion species within the limited interlayer space.[6] Here, we report the synthesis and characterisation of chain-like cationic Fe species within the interlayer of the montmorillonite, which showed an extremely high turnover number (TON) for the formation of cyclohexyl hydroperoxide in cyclohexane oxygenation using $H_2O_2$.

Fe ion-exchanged montmorillonite (Fe-mont) was prepared by the conventional ion-exchange of a parent Na$^+$-montmorillonite, $Na_{0.66}(OH)_4Si_{7.7}(Al_{3.34}Mg_{0.66}Fe_{0.19})O_{20}$ (1.0 g, Kunipia F, Kunimine Industry Co., Ltd.), with 50 mL of a $0.55 \times 10^{-3}$ M aqueous $Fe(NO_3)_3 \cdot 9H_2O$ solution. The slurry was washed with deionized water to ensure the removal of nitrate ions, followed by drying at 110 °C to give 0.90 g of an orange Fe-mont sample. Elemental analysis: Na, 0.1; Al, 11.0; Mg, 1.8; Fe, 4.4%. X-Ray photon spectroscopy (XPS): Fe $2p_{3/2}$ = 712.1 eV, FWHM = 5.26 eV; Si 2p = 102.4 eV, FWHM = 2.0 eV; Al 2p = 74.5 eV, FWHM = 1.9 eV, Mg 2s = 92.7 eV, FWHM = 3.0 eV; O 1s = 531.8 eV, FWHM = 2.3 eV, Fe:Al = 0.056. The peak position was referred to C 1s at 284.5 eV. The exchange degree of Na cations in the Fe-mont was 97.7%. Retention of the crystallinity was confirmed by its X-ray diffraction pattern, and the interlayer space was 2.2 Å which is smaller than that of the parent Na$^+$-mont (2.9 Å).

XPS and Fe K-edge XANES spectra confirmed a trivalent Fe species in the Fe-mont. As depicted in Fig. 1, the Fourier-transform of Fe K-edge EXAFS for the Fe$^{3+}$-mont was not similar to those for the bulk $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$, $Fe_3O_4$, and $Fe_2(SO_4)_3$, but is similar to that of $\alpha$-iron(III) hydroxide oxide ($\alpha$-FeOOH) with very small particle sizes.[†7,8] Curve-fitting analysis of peak I of the Fe$^{3+}$-mont showed that the cationic iron species had a coordination with two long Fe–O distances (2.03 Å) and two short Fe–O distances (1.90 Å), as summarized in Table 1. Each distance is slightly shorter than the values of 2.02 Å and 1.97 Å in the $\alpha$-FeOOH, respectively,[8] whereas it is longer than 1.86 Å found in the FeAlPO-5 molecular sieve, FePO$_4$, and Fe$^{3+}$-containing ZSM-5 wherein the Fe$^{3+}$ ions are monomerically situated in a tetrahedral coordination.[9] Peak II at 2.7 Å is assignable to an Fe–Fe moiety in the Fe$^{3+}$-mont; the interatomic distance between the two irons and the coordination

number are 3.05 Å and 2, respectively. The 3.05 Å Fe–Fe distance is associated with an Fe–Fe bond found in $\alpha$-FeOOH, where each Fe cation is bound by hydroxy groups at the corner.[8] Therefore, in the present Fe species, it is most likely that two Fe ions are bound by oxygen anions to form an $Fe_2(\mu\text{-O})_2$ core structure. Based on the above results, a coordination structure around iron species in the Fe$^{3+}$-exchanged montmorillonite is proposed as in Scheme 1, in which two Fe cations are linked by hydroxy anions along the interlayer space as a chain-like shape. To our knowledge, this is the *first* example of the synthesis of Fe cation linkages containing an Fe–O–Fe unit in the inorganic material by a simple ion-exchange method.‡ Such a linkage structure might be generated by a successive reaction of two neighboring iron hydroxides.[6b]

To explore the potential catalytic abilities of the above unique diiron species, liquid-phase oxygenation of cyclohexane using $H_2O_2$ was performed. Notably, the Fe$^{3+}$-mont showed a high catalytic activity for selective cyclohexane oxygenation to cyclohexyl hydroperoxide in the presence of trifluoromethanesulfonic acid (TFSA);§¶ a TON based on Fe ions reached 23 200 after 60 h (Scheme 2).
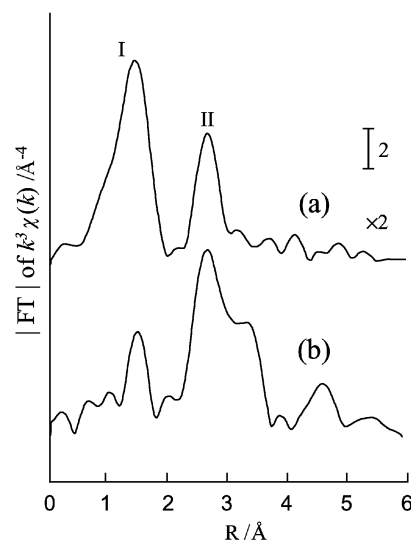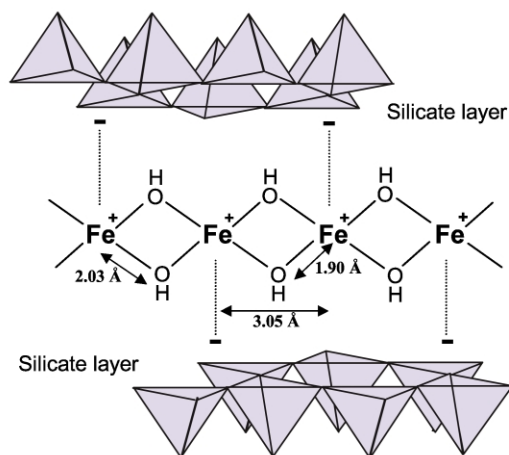


**Fig. 1** Fourier transforms for $k^3$-weighted Fe K-edge EXAFS of (a) Fe$^{3+}$-mont and (b) Fe$_2O_3$. Phase shift was not corrected.

**Table 1** Curve-fitting analysis for the Fe$^{3+}$-mont catalyst

| Shell | Coord. no. | Interatomic dist./Å | $\Delta\sigma^a$/Å$^2$ |
|---|---|---|---|
| Fe–O (1) | 2.0 | 1.90 | −0.0029 |
| Fe–O (2) | 2.0 | 2.03 | −0.0027 |
| Fe–Fe | 1.8 | 3.05 | −0.0005 |

$^a$ $\Delta\sigma$ is the difference between the Debye–Waller factor of the Fe$^{3+}$-mont and that of the reference sample.

**Scheme 1** Proposed schematic structure of $Fe^{3+}$ species within the interlayer space of montmorillonite. Two Fe ions are linked by two hydroxy anions to form an $Fe_2(\mu\text{-}O)_2$ core structure. The cationic Fe species are bound with anionic silicate layers.
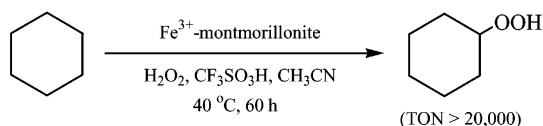


**Scheme 2**

The turnover frequency for $Fe^{3+}$-mont of 386 $h^{-1}$ is very much higher than those of 1.3, 2.4, 4, and 46 $h^{-1}$ for $[\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}]^{6-}$,[4] $Fe_2O(OAc)(tmima)_2^{3+}$ (tmima = tris[(1-methylimidazol-2-yl)methyl]amine),[2] $NaAuCl_4$,[11] and $VO(Hpda)_2(H_2O)$ (Hpda = pyrazine-2,3-dicarboxylic acid)[12] catalyst systems, respectively. It should be noted that the oxygenation was hardly catalysed by $Fe_2O_3$ under the present conditions.

One of the prominent characteristics of montmorillonites is an enlargement of the interlayer distance in polar solvents.[13] Indeed, the interlayer space of the $Fe^{3+}$-mont was expanded from 2.2 to 10.6 Å when soaked it in acetonitrile, as confirmed by its XRD pattern; most of Fe species within the interlayer become available for the oxygenation. Correspondently, the $Fe^{3+}$-mont catalyst system could also oxidise the larger cyclic alkane of cyclooctane to cyclooctyl hydroperoxide with a TON of 21 000 after 60 h.

The $Fe^{3+}$-mont catalyst was easily separated from the reaction mixture, and ICP analysis of the filtrate showed no leaching of Fe species during the above oxygenation. This catalyst could be reused four times keeping its high reaction rate and product selectivity for the oxygenation. When the filtrate was allowed to further react under the same conditions, oxygenation did not occur. Presumably, this alkane oxygenation might occur via a high valent oxoiron species, i.e. $Fe^{5+}=O$.‖ In the presence of TFSA, $H_2O_2$ oxidizes the $Fe^{3+}$–O–$Fe^{3+}$ species to give an $Fe^{5+}=O$ intermediate,[15] which reacts with cyclohexane, followed by attack of molecular oxygen to lead to the formation of cyclohexyl hydroperoxide and $Fe^{3+}$–OH.

In conclusion, a chain-like cationic Fe species can be created in the montmorillonite interlayer, which can act as a highly active catalytic site for the selective oxygenation of alkanes into the corresponding alkyl hydroperoxides using hydrogen peroxide in the presence of TFSA. The above simple preparation method using the cation-exchange ability of montmorillonite allows a strong protocol to create many metal ion linkages as unique heterogeneous catalysts.[6b]

## Notes and references

† In order to avoid an interference of Fe species initially presented within the silicate layer in the analysis, an EXAFS measurement was performed on the $Fe^{3+}$-mont sample prepared by using an Fe-free $Na^+$-mont. This material was synthesized according to the literature method. See: M. Shirai, K. Aoki, T. Miura, K. Torii and M. Arai, *Chem. Lett.*, 2000, 36. For curve-fitting analysis, the backscattering amplitudes and phase shift functions of Fe–O and Fe–Fe shells were obtained from $k^3$-weighted EXAFS of the CoO crystal (rock salt type, $a_0 = 4.26$ Å).[7]

‡ The interlayer distance of 2.2 Å for the $Fe^{3+}$-mont shows an incomplete crystal structure of Fe(III) hydroxides. A one-dimensional chain structure has been found in a divalent Fe complex consisting of an $[Fe^{2+}(Htrz)_3]$ unit (Htrz = 4H-1,2,4-triazole). See: T. Yokoyama, Y. Murakami, M. Kiguchi, T. Komatsu and N. Nojima, *Phys. Rev. B*, 1998, **58**, 14 238.

§ A typical procedure was as follows. Into a reaction vessel were successively placed the $Fe^{3+}$-mont (1.0 mg), $CH_3CN$ (100 mL), $CF_3SO_3H$ (0.35 mmol), cyclohexane (33 mmol), and 30% aq. $H_2O_2$ (12.5 mL, $H_2O_2$; 100 mmol). The mixture was stirred at 40 °C for 60 h under air. The $Fe^{3+}$-mont was separated by centrifugation. A molar ratio of cyclohexyl hydroperoxide : cyclohexanol in the filtrate was 7.4 : 1, which was confirmed by quantitative $^{13}C$ NMR measurements.[10] An aliquot of the filtrate was treated with an excess of triphenylphosphine at 50 °C.[10,11] GC analysis of the resulting solution gave 13.9 mmol of cyclohexanol. The TON was calculated from the above GC yield of cyclohexanol. From iodometry of the filtrate, the efficiency of $H_2O_2$ utilization based on consumed $H_2O_2$ (43 mmol) was 32%.

¶ In the cyclohexane oxygenation using $Fe^{3+}$-mont, the following reactivity of acids was observed: $CF_3SO_3H$ (23 200) > $CF_3COOH$ (9620) > $CH_3COOH$ (7360) >> no acid (5090). The values in parentheses are TONs. Without the $Fe^{3+}$-mont catalyst oxygenation did not occur, even in the presence of $CF_3SO_3H$.

‖ The kinetic isotope effect (KIE) was measured at the initial stage in the competitive oxygenation of an equimolar mixture of cyclohexane and cyclohexane-$d_{12}$ at 20 °C.[2,10] The KIE was observed to be 2.2, which is close to that of a 'Gif' oxidation system,[10] but different from that of a Fenton system.[14] The yield of oxygenated products under an Ar atmosphere was reduced to one-fifth of that obtained in air, suggesting a participation of gas phase oxygen in the oxygenation reaction.

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