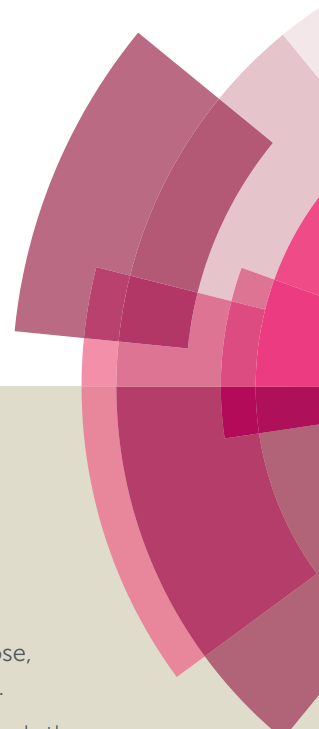


Catalysis Science & Technology

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: A. Pariyar, S. Bose, A. N. Biswas, S. Barman and P. Bandyopadhyay, *Catal. Sci. Technol.*, 2014, DOI: 10.1039/C4CY00453A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A Non-heme Cationic Fe(III)-complex Intercalated in Montmorillonite K-10: Synthesis, Characterization and Catalytic Alkane Hydroxylation with H₂O₂ at Room Temperature

Anand Pariyar,^a Suranjana Bose,^a Achintesh Narayan Biswas,^b Sudip Barman^c and Pinaki Bandyopadhyay^{*a}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

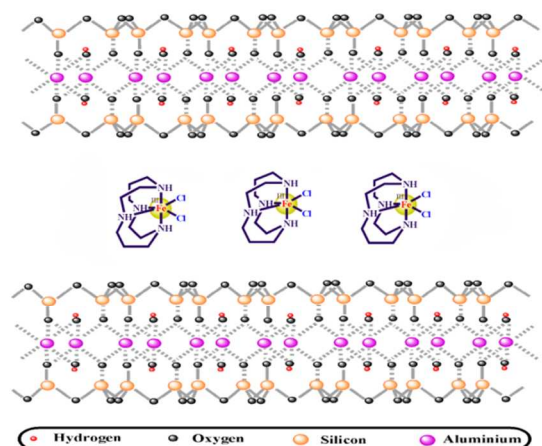
A non-heme iron complex *cis*-[Fe^{III}(cyclam)Cl₂]Cl (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been intercalated onto smectite montmorillonite K-10. The intercalated solid has been characterized using EDXRF, AAS, TGA, PXRD, IR and UV-visible analysis. The heterogeneous iron(III)-cyclam has been found to be capable of hydroxylating C-H bonds as strong as those in cyclohexane (BDE = 99.7 kcal/mol) using benign H₂O₂ at room temperature. The reactivity of the heterogeneous catalytic system is found to be significantly improved in comparison with that of *cis*-[Fe^{III}(cyclam)Cl₂]Cl/H₂O₂ under homogeneous condition. The catalytic reactions are marked by very high selectivity for alcohols which is comparable with the best known non-heme catalysts with H₂O₂. The results critically reflect the role of the clay matrix surrounding the cationic metal complex in tuning of catalytic activity and selectivity towards alkane hydroxylation.

Introduction

Catalytic hydroxylation of C-H bond in saturated hydrocarbons under mild conditions is a key step in the functionalization of many organic compounds and continues to be an important challenge.¹⁻⁵ There is always an increasing demand for more selective and efficient oxidation catalytic system in bulk as well as in fine chemical industries. Several challenges like selective conversion of methane to methanol,⁶ steroids hydroxylation,^{7,8} etc. are crucial with respect to alkane functionalization. An additional challenge is to make these transformations environmentally benign by using non-toxic reagents. Nature has devised an elegant solution to achieve selective activation of unactivated C-H bonds by employing metalloenzymes. Metalloenzyme catalyzed oxidation reactions operate under mild conditions and invariably exhibit very high stereo- and regioselectivity. The most extensively studied dioxygen activating metalloenzymes include cytochrome P-450, methane monooxygenase and Rieske dioxygenase.⁹⁻¹¹ Extensive research in these enzymatic processes have made significant advances in our understanding of how these enzymes work and stimulated research directed towards the design of synthetic oxidation catalysts. A number of biomimetic systems have been developed to model the reactivity of these enzymes.⁹⁻¹⁴ However, development of synthetically useful catalytic systems for stereospecific oxidation has largely remained elusive. The inability to achieve “enzyme-like activity” with the synthetic metal-based catalysts has often been attributed to the absence of protein chains as the high activity and selectivity of enzyme

catalyzed reactions are known to arise from protein mantle assisted spatial organisation of the reactants around the metal centre. Proteins, in metalloenzyme, accelerate chemical reactions by providing optimal binding and accessibility to substrates. It considerably improves solubility and facilitates target specific binding of substrate or an active species.¹⁵ Catalytic transformation occurs on substrate or solvent accessible surfaces and is strongly controlled by favoured molecular interactions. The strength and the structural precision of these interaction introduces affinity and specificity^{16,17} in the catalytic process. The role of protein matrix found in enzymes inspires chemist to incorporate size and shape selective framework of mineral matrix such as clays and zeolites, assuming that the mineral framework may generate optimal steric environment to provide specific binding site in catalytic systems, which, in turn, may help to achieve high specificity, stability and efficiency.¹⁸ In this context montmorillonite K-10, a non rigid smectite which has ion exchange properties and expands on intercalation may produce specific active centre for catalytic reaction.¹⁹ Although this technique have earlier been found successful as mimics for hydrocarbon activation using metalloporphyrin as active centres with PhIO by Barloy *et al.*,²⁰ the area still encourages us to go for more benign and hydrophilic H₂O₂. Moreover, diverse oxygenase activity of several non-heme enzymes prompted us to explore the catalytic reactivity of non-heme metal complexes trapped in size and shape selective framework. Herein, we wish to report the intercalation of an iron complex based on the tetrazacyclodecane ring *cis*-[Fe^{III}(cyclam)Cl₂]Cl (**1**) (cyclam = 1,4,8,11-tetraazacyclotetradecane)²¹ onto montmorillonite K-10 (**Mont**) (Scheme 1). The resulting intercalated solid has been fully

characterized and shown to perform selective C-H activation of unactivated alkanes with inexpensive and environmentally benign H_2O_2 at room temperature.



Scheme 1 Schematic diagram representing intercalation of **1**.

Experimental

Materials and Reagents

All chemicals were used as received unless noted otherwise. All the solvents used were of spectroscopic grade and were dried over 4 \AA molecular sieves before use. Montmorillonite K-10 & cyclam (1,4,8,11-tetraazacyclotetradecane) were procured from Sigma Aldrich and used as received. Active oxygen content of hydrogen peroxide was determined iodometrically prior to use.

Synthesis of *cis*-[Fe^{III}(cyclam)Cl₂]Cl (**1**)

Cis-[Fe^{III}(cyclam)Cl₂]Cl (**1**) was prepared by reacting cyclam with FeCl₂ in methanol following the literature method.²¹ Elemental Analysis (CHN): Anal. Cal. for C₁₀H₂₄N₄FeCl₃ : C, 33.13; H, 6.67; N, 15.45; Found: C, 33.30; H, 6.55; N, 15.40.

Intercalation of *cis*-[Fe^{III}(cyclam)Cl₂]Cl in Montmorillonite K-10 (**1-Mont**)

The intercalated catalyst was prepared by stirring a slurry of parent montmorillonite K-10 (1.0 g) with 100 mL aqueous solution containing 0.04 g *cis*-[Fe^{III}(cyclam)Cl₂]Cl for 15 h. The suspension was aged for 8 h. The suspension was filtered and washed thoroughly with water, methanol and acetonitrile. Finally the residue was dried in an oven at 100-120°C for 24 h giving the title solid.

Physical methods for characterization

X-Ray powder diffraction patterns were recorded with a computer-controlled Philips 1710 diffractometer (40 kV, 20 mA) equipped with a graphite monochromator. Diffractograms were collected from $2\theta = 5^\circ$ to 80° using steps of 0.02° (2θ) and a counting time of 0.5s per step. TGA analysis was studied using a locally made instrument Mettler thermobalance with a platinum pan. The samples were heated from 20 to 650°C at a ramp of 10°C per minute. EDXRF was performed with PAN analytical Epsilon 5. Scanning electron microscopy images were obtained on a JEOL JSM- 6360 scanning electron microscope (SEM) with an accelerating voltage of 20kV. AAS analysis was performed in Perkin Elmer 3110 Atomic Absorption Spectrometer. FT-IR

spectra were recorded with a Shimadzu model FTIR-8300 spectrometer, by transmission measurements of powdered samples mixed with KBr. UV absorption analysis of the solid sample was done making KBr pellets using JASCO V-530 spectrophotometer and the data was processed with built in spectra manager software. In all the experiments the scan speed was 400 nm/minute with a data pitch of 0.5nm. EPR analyses were done in Bruker BioSpin system with 9.4 GHz microwave frequency, 100 kHz modulation frequency, 5G modulation amplitude, 0.188 mW power and 2.8 minutes of sweep time. Magnetic susceptibility were recorded in Magnetic Susceptibility Balance, Sherwood Scientific, Cambridge, UK calibrated with HgCo(SCN)₄ ($g = 2$, $S = 3/2$). All the products of the oxidation reactions were analyzed in pre-heated Perkin Elmer Clarus 500 GC with FID (Polysiloxane, 15 m column).

Catalytic hydrocarbon oxidation

To a 1000 mM of substrate taken in a 5 mL vial equipped with a PTFE septum with cap containing 2 mL acetonitrile and given amount of catalyst were stirred at room temperature. The reaction was initiated by the addition of a given amount of H_2O_2 . In case of adamantane, 1000 mM substrate was taken in 2 mL 1:1 acetonitrile:dichloromethane due to solubility constrain. In a typical reaction, **1-Mont**/**Mont** = 12 mg (corresponding to 0.44 mM Fe), **1** = 1.0 mM and H_2O_2 = 22.0 mM. The reactions were monitored at regular intervals by removing 1 μL samples containing pre-added internal standard (dodecane) for GC analysis. Anaerobic reactions were carried by thoroughly flushing with argon prior to addition of substrate. Internal standard was added 1 h before the analysis done by GC. Products were analysed by comparing with calibrated curves of authentic samples of the product. All the substrates were checked by GC to ensure no oxidation product were present before the reaction. Reactions performed under identical condition in absence of catalyst or oxidant gave little or no product.

Results and Discussion

The immobilization of **1** has been developed by taking advantage of the ionic nature of the metal complex and ion-exchange ability of montmorillonite K-10. Intercalation is expected to be facilitated due to the presence of strong electrostatic interactions between the negatively charged layers of montmorillonite K-10 and the positively charged metal complex. The intercalation of **1** into montmorillonite K-10 has been achieved by stirring the constituents in water at room temperature, followed by filtration, washing and drying. The intercalated solid was washed thoroughly with H_2O , MeOH and CH_3CN respectively to remove any free complex or neutral ligand. Elemental analysis of **1-Mont** by EDXRF shows Si, 15.9; Al, 3.7; Mg, 0.4; Fe, 1.2%. The net increase in the iron-content in the intercalated product **1-Mont** was estimated to be 0.4% (w:w) which accounts for 2.7% (w:w) intercalation of **1** into montmorillonite K-10. This result is further supported by atomic absorption spectroscopy (AAS) data and thermo gravimetric analysis (TGA) profile. TGA profile of **1-Mont** (Fig. 1) shows that it contains 7% (w/w) of additional water than that of parent montmorillonite K-10. The high thermal stability of **1-Mont** compared to the complex **1** is evidenced by the high temperature (500-700°C) required to eliminate the

organic moiety associated with the clay. In contrast, rapid weight loss corresponding to the combustion of cyclam is observed in case of complex **1** within temperature range of 200-500°C. Comparison of electronic spectra of the clay and the intercalated solid (**1-Mont**) also demonstrate that *cis*-[Fe^{III}(cyclam)Cl₂]Cl (**1**) is held intact within the interlayers of Montmorillonite K-10. The derivative UV-visible spectrum of the iron(III) complex (**1**) (ESI,† Fig. S1) exhibits an absorption at 233 nm. The intercalated solid (**1-Mont**) displays a similar absorption at 230 nm indicating the presence of **1** within the clay matrix. Notably, Montmorillonite K-10 itself is devoid of any such absorption in this region.

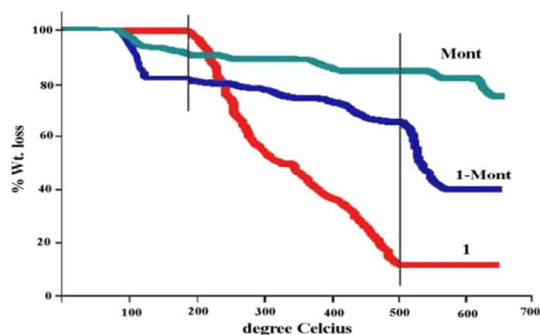


Fig. 1 TGA profiles of montmorillonite K-10 (**Mont**), **1-Mont** and **1**.

Intercalation of **1** into Montmorillonite K-10 has further been confirmed by X-ray diffraction (XRD) studies. The X-ray diffraction pattern (ESI,† Fig. S2) of the parent Montmorillonite K-10 clay shows a basal (d_{001}) spacing of 9.56 Å along the c-axis at approximately 9.0° (2θ), indicating a layered structure. The XRD pattern of the solid after intercalation of **1** into the clay matrix (**1-Mont**) display an expansion of the basal spacing to 10.15 Å (2θ = 8.71°). Similar expansion of the basal spacing of smectic clays was reported in intercalated Mn-porphyrins and cobalt ammine complexes.²² Parallel orientation of these complexes inside the layered structures has been proposed to explain the basal expansion. Therefore, it is reasonable to believe that the expansion of the basal spacing observed in case of **1-Mont** can be attributed to the parallel orientation of **1** inside the clay sheets (Scheme 1).

The FT-IR-spectra of the parent montmorillonite K-10 clay, iron(III)cyclam complex (**1**) and the intercalated catalyst (**1-Mont**) are compiled in the Supporting Information (ESI,† Fig. S3). In case of the parent clay, characteristic vibrational band at 3428 cm⁻¹ corresponding to the stretching vibrations of interlayer water molecules is observed. Consistent with the earlier studies on metal complex intercalation in Montmorillonite,²³ the band has been found to be shifted to 3445 cm⁻¹ after intercalation of the iron(III) complex. Vibrational features at 462 and 524 cm⁻¹ corresponding to the Si-O bending vibrations²⁴ in Montmorillonite have also been shifted to 472 and 529 cm⁻¹ upon intercalation. Broad and intense asymmetric Si-O stretching vibration is observed around 1050 cm⁻¹, which in turn, overlaps with the bands of complex **1** in that region. Scanning electron microscope (SEM) images of montmorillonite K-10 and **1-Mont** (Fig. 2) show similar flake-like morphology supporting successful intercalation. Finally, an EPR investigation has been undertaken in order to examine any structural change of the

iron(III) complex upon intercalation (ESI,† Fig. S4). Solid state EPR spectrum of complex **1** at 77K (g = 9.0 and 4.01) is characteristic of a high-spin complex with axial symmetry.²¹ However, the signal at g = 2 is not observed at 77K. The EPR spectrum of the solid catalyst (**1-Mont**) has been found to be identical with that of **1** confirming that the complex **1** retains its structure within the clay matrix. Moreover, the presence of high-spin Fe(III) centres (S = 5/2) within the solid intercalated solid is also consistent with its magnetic susceptibility data ($\mu_{\text{eff}} = 5.9 \mu_B$).

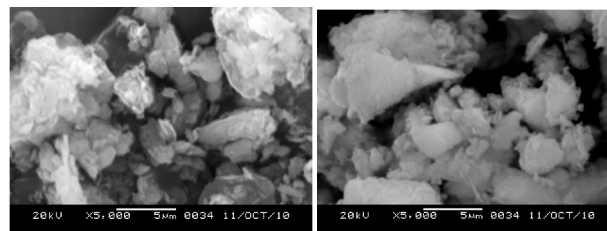


Fig. 2 SEM micrograph of montmorillonite K-10 (Left) & **1-Mont** (Right).

The non-heme tetrazacyclotetradecane ring based iron complex **1** offers two potential *cis*-coordination sites which has been shown to be one of the prerequisite for dioxygen activation.²⁵ Therefore, the catalytic property of complex **1** with H₂O₂ has been evaluated towards alkane hydroxylation. Only 6-7% yield of oxygenates with alcohol to ketone ratio (A/K) of 1.0 is obtained with excess alkane concentration (Table 1). In contrast, the solid supported **1-Mont** has been found to be an excellent catalyst for selective alkane hydroxylation with H₂O₂ as the oxidant. In a typical reaction, 12 mg of the intercalated solid which corresponds to 0.44 mM iron(III), has been used. The catalytic reactions were performed using H₂O₂ as the limiting reagent (Fe/H₂O₂/substrate = 1:50:1000). In case of cyclohexane, cyclohexanol was obtained as the exclusive product with overall yield of 45% (22 turnovers) based on the oxidant concentration. The alkane hydroxylation reactions catalyzed by **1-Mont**/H₂O₂ have been monitored as a function of time (ESI,† Figure S5-S7). Formation of alcohols is found to be completed in 20 h and appeared to be exponential. The results clearly exclude any possibility of over-oxidation in the present catalytic system. Moreover, the heterogeneous catalyst was recovered by filtration at the end of the reaction and characterized by powder XRD. The X-ray diffraction patterns of the catalyst before and after the reaction have been found to be similar albeit an expansion of the basal spacing from 10.15 Å to 10.27 Å. Cycloalkane oxidation catalyzed by Fe³⁺-intercalated montmorillonite with H₂O₂ is known to yield organohydroperoxide (ROOH) as the exclusive product. However, the oxidation requires the presence of trifluoromethanesulfonic acid (TFSA) and elevated temperature.²⁶ In contrast, the present catalytic system provides cyclohexanol directly as the exclusive product at room temperature (Entry 3, Table 1). Furthermore, the present catalytic system converts C-H to C-OH at room temperature without the requirement of any additives in the form of corrosive acid or reductants. Under similar reaction condition, cyclooctane was converted to cyclooctanol with 35% yield with very high selectivity for alcohol and adamantane has been found to be hydroxylated to a mixture of 1-adamantanol and 2-adamantanol with an overall yield of 51%. Not even a trace amount of ketone (2-adamantanone) is detected. Normalised 3°/2°

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table 1 Oxidation of alkanes at room temperature with H₂O₂^a

Entry	Substrate	Catalyst	Yield ^b	Remark	% Selectivity			
					A/K ^d	Cyclohexanol	Cyclohexanone	
1	Cyclohexane	1	6	1.0	50	50		
2		Mont	26	1.0	50	50		
3		1-Mont	45	49.0	98		2	
					A/K ^c	Cyclooctanol	Cyclooctanone	
4	Cyclooctane	1	07	1.0	50	50		
5		Mont	66	1.1	52	48		
6		1-Mont	35	32.0	97		3	
					3°/2° ^d	1-Adamantanol	2-Adamantanol	2-Adamantanone
7	Adamantane	1	15	15.7	84	8	8	
8		Mont	97	11.3	79	14	7	
9		1-Mont	51	27.0	90	10	0	

^a See experimental section for reaction conditions; ^b Yield with respect to oxidant concentration; ^c A/K= alcohol/ketone ratio; ^d 3°/2° values have been normalized per hydrogen basis using the formula $[1\text{-adamantanol}/(2\text{-adamantanol}+2\text{-adamantanone})] \times 3$.

ratio (see footnote of Table 1 for details) of 28.7 has been obtained for adamantane. Selective hydroxylation with 3°/2° ratio of 28.7 shows very high relevance to biomimetic Cytochrome P-450 oxygenating system.²⁷ It is noteworthy that only a very few nonheme iron catalysts have displayed such high selectivity in adamantane hydroxylation.²⁸ It is thus reasonable to believe that the hydroxylation of alkanes occur *via* high-valent iron oxospecies. Selectivity towards the hydroxy derivatives of adamantane has been found to be better than that obtained with vanadium exchanged montmorillonite K-10 in *tert*-butyl acetate solvent under an oxygen atmosphere.²⁹ Vanadium intercalated montmorillonite catalyzed oxygenation of adamantane afforded 1-adamantanol, 1,3-adamantanediol and 2-adamantanone in 41 : 44 : 15 ratio.

Since montmorillonite clays are itself known to possess significant catalytic reactivity,³⁰ alkane hydroxylation reactions have been performed with the parent clay to determine the origin of selectivity in the present case. As shown in Table 1, montmorillonite K-10 under identical reaction condition yields 26% oxygenates in case of cyclohexane oxidation with equimolar amounts of alcohols and ketones. Much higher alcohol selectivity in case of the immobilized catalyst compared with the parent clay is clearly indicative of the fact that the intercalated iron(III) complex affects the reactivity presumably by controlling the access of the substrate and oxidant to the metal centres, which, in turn, improves the selectivity of the overall process. Furthermore, control experiments are also performed with iron(III) nitrate intercalated montmorillonite with H₂O₂ and the results obtained in agreement with the earlier study.³¹ Therefore, the above results critically reflect the role of clay matrix surrounding the cationic metal complex in tuning of catalytic activity and selectivity of alkane hydroxylation.

Furthermore, in an attempt to evaluate the synthetic potential of the heterogeneous system, cyclohexane hydroxylation reactions

have been performed in substrate limiting condition (substrate = 2.5 mM) (ESI,† Table S1-S3). Experiments with increasing **1-Mont** concentration and constant H₂O₂ (5 mM) & cyclohexane (2.5 mM) shows that albeit lower substrate conversion (5%), alcohol is formed exclusively and the yield increases with increase in catalyst (**1-Mont**) concentration. However, loss of selectivity on increasing H₂O₂ concentration over 4.0 equivalent of that of substrate was observed with the formation of small amount of cyclohexanone (A/K = 2.3). The results (ESI,† Table S1-S3) elaborate the role of all three components (substrate, catalyst and oxidant) over product selectivity. The loss of selectivity on increasing H₂O₂ concentration may be due to the alteration of oxidising species or the over-oxidation of alcohols on increased oxidant concentration.^{32,33}

The mechanisms for hydrocarbon oxidation catalyzed by non-heme iron complexes have attracted significant interest in the chemical and biochemical communities. In case of mononuclear iron(II) catalysts, dioxygen activation has been shown to proceed *via* either iron(III)-peroxo or high-valent iron oxo intermediates.^{25,34-39} However, several non-heme iron complexes have also been shown to follow a typical free radical pathway.⁴⁰⁻⁴⁵ In contrast, Shulpin *et al.* invoked the involvement of hydroxyl radicals in oxidation of alkanes by solid montmorillonite.⁴⁶ Superior alkane hydroxylating ability of the immobilized catalyst (**1-Mont**) together with very high selectivity for alcohols univocally exclude the involvement of radicals in the present catalytic system. This is further confirmed by the fact that **1-Mont**/H₂O₂ catalyzed alkane hydroxylation reactions remain unaffected in presence of radical scavenger. However, almost complete suppression of the oxidative reactivity of the solid support (Montmorillonite K-10) as well as the iron(III) complex (**1**) in the heterogeneous catalyst (**1-Mont**) deserves special mention. In order to understand the origin of this unique reactivity pattern, the rate of cyclohexane oxidation catalyzed by

1-Mont has been compared with those catalyzed by the iron(III) complex (**1**) and solid montmorillonite K-10 (ESI,† Figure S8). The method of initial rate has been used to limit interferences such as decomposition of H₂O₂, swelling of the clay by the reaction products and inactivation of the catalyst. The values for second-order rate constants calculated for cyclohexane oxidation by **1**/H₂O₂, **Mont**/H₂O₂ and **1-Mont**/H₂O₂ have been found to be 1.18 × 10⁻⁴, 2.0 × 10⁻⁴ and 9.74 × 10⁻⁴ M⁻¹h⁻¹ respectively. Therefore, the intercalated catalyst (**1-Mont**) accelerated the rate of cyclohexane oxidation almost ten times with respect to that found for the free catalyst. The reaction rate is also considerably faster (five times) when compared with the rate calculated for the clay support. The data show the generation of a new active heterogeneous catalyst and its enhanced selective may be attributed to a favourable cooperative interaction between its constituents. It is likely that upon intercalation, water molecules displace the iron(III) bound chlorides, thereby making the coordination sites more accessible for H₂O₂. Although, more rigorous mechanistic work is needed to fully understand the catalytic system, the present work evolves as a useful strategy to generate selective hydroxylation catalysts by immobilizing catalytically potent iron complex into size and shape selective framework of montmorillonite clay.

Conclusions

The non-heme iron(III) complex, *cis*-[Fe^{III}(cyclam)Cl₂]Cl (**1**) has been successfully immobilized in montmorillonite clay. The resulting intercalated solid (**1-Mont**) is characterized using powder EDXRF, AAS, TGA, XRD, IR and UV-visible analysis. Elemental analysis of **1-Mont** by EDXRF as well as atomic absorption spectroscopy (AAS) showed 2.7% (w/w) intercalation of the complex **1** into montmorillonite K-10. Catalytic reactivity of **1-Mont**/H₂O₂ towards hydroxylation of alkanes at ambient condition was evaluated. **1-Mont** emerged as an efficient catalyst for highly selective hydroxylation of alkanes using environmentally benign H₂O₂ at room temperature. The catalytic reactivity of the complex **1** has been shown to improve dramatically upon its intercalation into the clay material. Inert alkanes such as cyclohexane (BDE = 99 kcal/mol) and cyclooctane (BDE = 96 kcal/mol) were oxidized to the corresponding hydroxyalkanes almost exclusively. The reaction profile showing high alcohol selectivity rules out the involvement of freely diffusing radicals in the present case and indicates the involvement of high-valent iron-oxo species as intermediates. The results suggest that the present oxidation system studied has potential for commercial exploitation and particularly important for its environment friendly nature. Moreover, the work also provides a useful strategy to improve the selectivity of several non-heme catalytic systems operating under homogeneous conditions. Further studies aimed at developing a practical, synthetically useful catalytic systems based on **1-Mont**/H₂O₂ are in progress in the laboratory.

Acknowledgements

The financial support from SERB (SR/S1/IC-53/2010), DST, Government of India and CSIR (1/2498/11/EMR-II) and University Grants Commission [F. No. 42-324/2013(SR)], New

Delhi are gratefully acknowledged. We thank CSIR (India) for the award of fellowships to AP & SB and SAIF-NEHU, Shillong for AAS and SEM analysis. The authors would like to thank the reviewers for their valuable suggestions.

Notes and references

- ^a Department of Chemistry, University of North Bengal, Siliguri 734013, West Bengal, India, Fax: 91-353-2699001; E-mail: chempb@gmail.com
^b Department of Chemistry, Siliguri College, Siliguri 734001, West Bengal, India; E-mail: achintesh@gmail.com
^c School of Chemical Science, National Institute of Science Education and Research (NISER), Bhubaneswar, Orissa 751005, India.
 † Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/
- J. W. Delord and F. Glorius, *Nat. Chem.*, 2013, **5**, 369-375.
 - R. G. Bergman, *Nature*, 2007, **446**, 391-393.
 - K. Godula and D. Sames, *Science*, 2006, **312**, 67-72.
 - J. A. Labinger and J. E. Bercaw, *Nature*, 2002, **417**, 507-514.
 - R. H. Crabtree, *J. Chem. Soc. Dalton Trans.*, 2001, 2437-2450.
 - C. Hammond, M. M. Forde, Mohd. H. Ab Rahim, A. Thetford, Q. He, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, N. F. Dummer, D. M. Murphy, A. F. Carley, S. H. Taylor, D. J. Willock, E. E. Stangland, J. Kang, H. Hagen, C. J. Kiely, G. J. Hutchings, *Angew. Chem. Int. Ed.*, 2012, **51**, 5129-5133.
 - D. Zehentgruber, C. A. Drăgan, M. Bureik and S. Lütz, *J Biotechnol.*, 2010, **146**, 179- 85.
 - P. Fernandes, A. Cruz, B. Angelova, H. M. Pinheiro and J. M. S. Cabral, *Enzyme Microb. Technol.*, 2003, **32**, 688-705.
 - S. Friedle, E. Reisner and S. J. Lippard, *Chem. Soc. Rev.*, 2010, **39**, 2768-2779.
 - W. Nam, *Acc. Chem. Res.*, 2007, **40**, 465-634.
 - C. E. Tinberg and S. J. Lippard, *Acc. Chem. Res.*, 2011, **44**, 280-288.
 - L. Que Jr. and W. B. Tolman, *Nature*, 2008, **455**, 333-340.
 - M. Costas, K. Chen and L. Que Jr., *Coord. Chem. Rev.*, 2000, **200-202**, 517-544.
 - G. A. Russell, *The Chemistry of alkanes and cycloalkanes*, (Eds. S. Patai and Z. Rappoport) Wiley, New York, 1992, pp. 966.
 - D. Voet, J. G. Voet, and I. Geis, *Biochemistry*, 2nd edition, Wiley New York 1995.
 - A. Gunnarsson, P. Jönsson, V. Zhdanov and F. Höök, *Nucleic Acids Research*, 2007, **37**, e99 (1-8).
 - A. M. Levina and G. A. Weiss, *Mol. BioSyst.*, 2006, **2**, 49-57.
 - J. P. Collman, X. Zhang, V. J. Lee, U. S. Uffelman and J. I. Brauman, *Science*, 1993, **261**, 1404-1411 and references therein.
 - Z. Li, R. Tang and G. Liu, *Catal Lett.*, 2013, **143**, 592-599.
 - L. Barloy, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1990, 1365-1367.
 - R. Guillard, O. Siri, A. Tabard, G. Broeker, P. Richard, D. J. Nurco and K. M. Smith, *J. Chem. Soc. Dalton Trans.*, 1997, 3459-3463.
 - F. Bedioui, *Coord. Chem. Rev.*, 1995, **144**, 39-68.
 - C. V. Rode, V. S. Kshirsagar, J. M. Nadgeri and K. R. Patil, *Ind. Eng. Chem. Res.*, 2007, **46**, 8413-8419.
 - N. N. Binitha and S. Sugunana, *Microporous Mesoporous Mater.*, 2006, **93**, 82-89.
 - M. Costas, M. P. Mehn, M. P. Jensen and L. Que, Jr., *Chem. Rev.*, 2004, **104**, 939-986.
 - K. Ebitani, M. Ide, T. Mitsudome, T. Mizugaki and K. Kaneda, *Chem. Commun.*, 2002, 690-691.
 - P. R. Ortiz de Montellano, *Cytochrome P450: Structure, Mechanism and Biochemistry*, 3rd edition, Kluwer Academic/Plenum Publishers, New York, 2005.
 - A. Company, L. Gomez, M. Guell, X. Ribas, J. M. Luis, L. Que, Jr., M. Costas, *J. Am. Chem. Soc.* 2007, **129**, 15766-15767.
 - T. Mitsudome, N. Nosaka, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem. Lett.*, 2005, **34**, 1626-1627.
 - J. P. Ferris, A. R. Hill Jr., R. Liu and L. E. Orgel, *Nature*, 1996, **381**, 59-61.

- 31 U. R. Pillai, E. S. Demessie, *Appl. Catal. A: General*, 2003, **245**, 103-109.
- 32 A. Pariyar, S. Bose, A. N. Biswas, P. Das and P. Bandyopadhyay, *Catal. Commun.*, 2013, **32**, 23-27.
- 5 33 N. A. Stephenson and A. T. Bell, *J. Am. Chem. Soc.*, 2005, **127**, 8635-8643.
- 34 A. L. Nivorozhkin and J. -J. Girerd, *Angew. Chem.*, 1996, **108**, 665-667; *Angew. Chem. Int. Ed.*, 1996, **35**, 609-611
- 35 M. M. Abu-Omar, A. Loaiza and N. Hontzeas, *Chem. Rev.*, 2005, 10
105, 2227-2252.
- 36 M. Fontecave, S. Menage and C. Duboc-Toia, *Coord. Chem. Rev.*, 1998, **178-180**, 1555-1572.
- 37 S. V. Kryatov, E. V. Rybak-Akimova and S. Schindler, *Chem. Rev.*, 2005, **105**, 2175-2226.
- 15 38 C. Kim, K. Chen, J. Kim and L. Que, Jr., *J. Am. Chem. Soc.*, 1997, **119**, 5964-5965.
- 39 K. Chen and L. Que, Jr., *J. Am. Chem. Soc.*, 2001, **123**, 6327-6337.
- 40 R. A. Leising, J. Kim, M. A. Perez and L. Que, Jr., *J. Am. Chem. Soc.*, 1993, **115**, 9524-9530.
- 20 41 J. Kim, C. Kim, R. G. Harrison, E. C. Wilkinson and L. Que, Jr., *J. Mol. Catal.*, 1997, **117**, 83-89.
- 42 A. Bassan, M. R. A. Blomberg, Per E. M. Siegbahn and L. Que, Jr., *Angew. Chem. Int. Ed.*, 2005, **44**, 2939-2941.
- 43 R. H. Fish, M. S. Konings, K. J. Oberhausen, R. H. Fong, W. M. Yu, 25
G. Christou, J. B. Vincent, D. K. Coggin and R. M. Buchanan, *Inorg. Chem.*, 1991, **30**, 3002-3006.
- 44 R. M. Buchanan, S. Chen, J. F. Richardson, M. Bressan, L. Forti, A. Morvillo and R. H. Fish, *Inorg. Chem.*, 1994, **33**, 3208-3209.
- 45 M. Kodera, H. Shimakoshi and K. Kano, *J. Chem. Soc., Chem. Commun.*, 1996, 1737-1738.
- 30 46 D. Mandelli, A. C. N. do Amaral, Y. N. Kozlov, L. S. Shul'pina, A. J. Bonon, W. A. Carvalho and G. B. Shul'pin, *Catal. Lett.*, 2009, **132**, 235-243.