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Selective alkane hydroxylation and alkene epoxidation using H₂O₂ and Fe(II) catalysts electrostatically attached on fluorinated surface[†]

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Fe(II) complexes having pentadentate ligands including *N*-heterocyclic carbene moieties were prepared and electrostatically attached on the perfluorinated surface of a mesoporous aluminosilicate. The heterogeneous catalysts were applied to catalytic oxidation of cyclohexane and cyclohexene using H₂O₂ as an oxidant in CH₃CN, demonstrating high performance and selectivity in alkane hydroxylation and cyclohexene epoxidation.

Hydroxylation of alkanes as well as epoxidation of alkenes using metal complexes as catalysts and hydrogen peroxide (H₂O₂) as a “green” oxidant should be of great importance in terms of atom economy as an oxidant and no production of hazardous wastes.¹ However, in use of H₂O₂ as an oxidant for metal-catalysed oxidation reactions, radical chain reactions are often involved through so-called Fenton reactions, making the reactions less selective.² On the contrary, selective catalytic oxidation of organic compounds has been developed on the basis of the formation of high-valent Fe-oxo complexes as responsible species from the reaction of H₂O₂ with Fe^{II} complexes;³ however, suppressing over-oxidation of 2e⁻-oxidized products still needs to be considered.

In order to suppress over-oxidation of 2e⁻-oxidized products, hydrophobic micro-environment around metal complexes as catalysts would be effective to gain efficiency and selectivity of oxidation of hydrophobic compounds in polar media.⁴ In addition, in order to improve the durability of oxidation catalysts, it should be useful to fix the catalysts on a surface of a support, making the catalyst heterogeneous to avoid decomposition due to intermolecular reaction between

the reactive intermediate and the catalyst. Aluminosilicates, in which a portion of the Si atoms in the SiO₂ framework is replaced by Al, possess protons for charge compensation derived from the difference in the number of valence electrons between silicon and aluminum. Taking advantage of the fact that these protons can be exchangeable with other cationic species, the aluminosilicates have been used as a robust support for converting cationic complexes that function as homogeneous catalysts into heterogeneous solid catalysts.⁵ So far, Fukuzumi and coworkers have reported on the immobilization of metal complexes as catalysts in a mesoporous aluminosilicate, Al-MCM-41, to achieve selective oxidation of benzene to phenol using H₂O₂ as an oxidant;⁶ however, no example has been reported on the introduction of hydrophobic environment on the surface of aluminosilicates as the support of catalysts for the preparation of heterogeneous metal-complex catalysts. Thus, we have developed a heterogeneous catalyst consisting of Fe(II) complexes having pentadentate ligands with *N*-heterocyclic carbene (NHC) moieties as catalysts⁷ and a hydrophobized mesoporous aluminosilicate with fluorinated alkyl chains and negatively charged sites that interact electrostatically with positively charged catalysts to fix those catalysts.

Herein, we describe selective hydroxylation of cyclohexane (CyH) and epoxidation of cyclohexene (Cyene) in water using

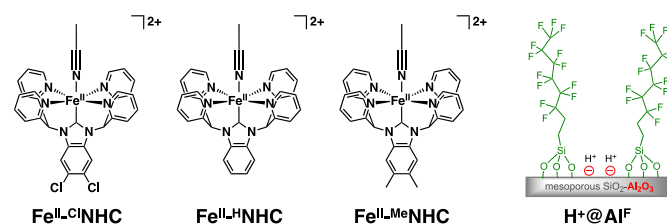


Fig. 1 Schematic representation of Fe^{II}-ClNHC, Fe^{II}-HNHC, Fe^{II}-MeNHC and H⁺@AlF. FC: (CF₂)₃CF₃.

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aqueous H₂O₂ (30%) as an oxidant and Fe^{II}-NHC complexes immobilized on the hydrophobic fluorinated solid surface as catalysts. In this study, we have developed heterogeneous oxidation catalysts using PF₆⁻ salts of Fe^{II}-NHC complexes, Fe^{II}-^{Cl}NHC,⁶ Fe^{II}-^HNHC and Fe^{II}-^{Me}NHC and an SBA-15 type mesoporous aluminosilicate bearing hydrophobic surface decollated by perfluorinated C₆ chains, fluoroalkyl-functionalized Al-SBA-15. The three complexes are fixed on the surface based on electrostatic interaction to afford Fe^{II}-^{Cl}NHC@AlF, Fe^{II}-^HNHC@AlF and Fe^{II}-^{Me}NHC@AlF, respectively, as catalysts for hydrocarbon oxidation (Fig. 1; abbreviations: ^{Cl}NHC, 5,6-dichloro-1,3-dihydro-methyl-2H-benzimidazol-2-ylidene; ^HNHC, 1,3-dihydro-1,3-bis(2-pyridyl)-methyl-2H-benzimidazol-2-ylidene; ^{Me}NHC, 5,6-dimethyl-1,3-dihydro-1,3-bis(2-pyridyl)-methyl-2H-benzimidazol-2-ylidene; **H⁺@AlF**, C₆F₁₃-C₂H₄-functionalized Al-SBA-15).

Synthesis of all complexes are described in the ESI†. Characterization of Fe-^{Cl}NHC was described in our previous report.⁸ Fe-^HNHC and Fe-^{Me}NHC were characterized by ¹H NMR (Figs. S1 and S2 in the ESI) and UV-vis absorption spectroscopies, ESI-TOF-MS spectrometry (Figs. S3 and S4 in the ESI) and elemental analysis. The precursor of the hydrophobic support, Al-SBA-15, was prepared according to the procedure reported by Krishana and Selvam with some modifications.⁸ Its surface area, pore size distribution, and pore volume derived from the N₂ adsorption isotherm curves were consistent with the characteristics of SBA-15 type mesoporous support (Fig. S5 in the ESI). Anchoring the triethoxy-1H,1H,2H,2H-tridecafluoro-*n*-octylsilane on the surface of Al-SBA-15 yielded **H⁺@AlF**. The hydrophobic nature of **H⁺@AlF** was evidenced by a large contact angle of H₂O (Fig. S6 in the ESI). Immobilization of the Fe complexes was performed by cation-exchange of **H⁺@AlF** with PF₆⁻ salts of the Fe^{II}-NHC complexes (Fig. 1) in acetonitrile. The details of synthetic processes are provided in the ESI†. The characterization of Fe-^RNHC@AlF (R = Cl, H, Me) was performed by UV-vis-NIR reflectance spectroscopy (Figs. S7–S9 in the ESI). The loadings of Fe complexes on AlF for Fe^{II}-^{Cl}NHC@AlF, Fe^{II}-^HNHC@AlF and Fe^{II}-^{Me}NHC@AlF were calculated to be 7.3, 16, 23 nmol mg⁻¹, respectively, based on the ¹H NMR spectroscopy. The details of determination of loadings of Fe complexes are provided in the ESI†.⁹ The tendency of the amount of Fe complexes indicates that Fe^{II}-^{Me}NHC@AlF shows the largest loading amount among the three Fe complexes owing to the δ⁻ property of the surface of AlF and the δ⁺ property of the

surface of methyl substituents on the benzimidazole moiety.

Catalytic oxidation was performed in a glass tube containing CD₃CN (1.0 mL), Fe^{II}-^RNHC@AlF (10 nmol, R = Cl, H, Me), H₂O₂ as an oxidant (16 mM) and a substrate (100 mM) at 313 K under Ar atmosphere. The turnover numbers (TONs) after stirring for 3 h were determined by ¹H NMR spectroscopy. In the CyH oxidation, we could observe the formation of cyclohexanol (Cy-OH) and cyclohexanone (Cy=O) as two-electron- and four-electron-oxidised products, respectively. As a catalyst, Fe^{II}-^{Cl}NHC@AlF showed the highest total TON of 744 among the three catalysts applied. We also performed the CyH oxidation in trifluoroethanol instead of acetonitrile to investigate the solvent effects; however, any oxidation product was not detected (Table S1). This result indicates that a protic solvent is not suitable for the oxidation reactions reported herein. The high alcohol/ketone (A/K) ratios indicate that Fe^{II}-^RNHC@AlF selectively catalyses 2e⁻ oxidation of CyH by suppression of overoxidation owing to the hydrophobic fluorinated surface of AlF. Among the three catalysts, Fe^{II}-^{Cl}NHC@AlF showed 95% selectivity. It should be noted that Fe^{II}-^RNHC complexes as homogeneous catalysts and the support **H⁺@AlF** showed 100-fold lower catalytic activity and no reactivity in CyH oxidation with H₂O₂ (Table S2).

To gain a mechanistic insight into the catalytic C-H oxidation using Fe^{II}-^{Cl}NHC@AlF, we employed cumene, toluene and cyclooctane as substrates. The total TONs (3 h) of the oxidation reaction for cumene, toluene and cyclooctane were 1430, 1155, 855 (Tables 1 and S3). The A/K ratios for toluene, cyclooctane were 20 and 23, which is comparable to that (18) of CyH (Tables 1 and S3). We also employed *cis*-1,2-dimethylcyclohexane as a substrate to investigate the stereochemistry of the product upon hydroxylation in an Fe^{IV}=O-mediated mechanism. The oxidation of *cis*-1,2-dimethylcyclohexane afforded only *cis*-1,2-dimethylcyclohexan-1-ol with complete stereo-retention in TON of 420.¹⁰ The stereo-retention is more complete than that reported for high-valent nonheme Fe=O complexes.^{3a} These results indicate that the catalytic oxidation reaction by using Fe^{II}-^RNHC@AlF as a catalyst and H₂O₂ as an oxidant in acetonitrile should be conducted not by free radicals derived from H₂O₂ but by Fe^{IV}=O intermediates. In addition, we performed a competitive catalytic oxidation reaction using an equimolar mixture of cyclooctane and Cy-OH (50 mM each) as a substrate. The oxidation of the mixture afforded mainly cyclooctanol with the total TON 780 (Table S4), which is comparable to that (855) of cyclooctane oxidation (Table S3); Cy=O was also obtained as a minor product from Cy-OH with a low TON of 20. This clearly indicates that alkane oxidation is more preferable than alcohol oxidation in our catalytic system owing to the hydrophobic surface of AlF even if Cy-OH has the lower BDE_{C-H} than cyclooctane. High alcohol selectivity has been reported for C-H oxidation in strong hydrogen-bond-donor solvents such as fluoroalcohols which deactivate alcohols.¹¹ On the contrary, our catalytic system has achieved high alcohol selectivity even in CH₃CN owing to the hydrophobic micro-environment where hydrophobic alkanes are favourably incorporated and hydrophilic alcohols are eliminated.

To investigate the durability of Fe^{II}-^RNHC@AlF catalysts, the

Table 1. Catalytic oxidation of cyclohexane by H₂O₂ (30% aq) and Fe-^RNHC@AlF in CH₃CN under Ar.

R	Product	TON ^a	Alcohol/Ketone
Cl	Cy-OH	705	18
	Cy=O	39	
H	Cy-OH	468	11
	Cy=O	43	
Me	Cy-OH	329	7
	Cy=O	50	

^aTONs = [Product]/[catalyst]. Conditions: catalyst: 10 nmol, [H₂O₂] = 16 mM, [substrate] = 100 mM, T = 313 K, and reaction time = 3 h. TONs were determined by GC-MS spectroscopy. Any side-reaction products except those listed in the table were not observed.

recycling test for the heterogeneous Fe^{II} catalysts in CyH oxidation was examined under the same conditions. After the 1st catalytic CyH oxidation reaction, the solid catalyst was collected by centrifugation and washed by acetonitrile five times. As for the 2nd–5th catalytic CyH oxidation reactions, each run was performed to determine the amount of each product by GC analysis after the determination of the amount of the corresponding Fe catalyst retained on the surface by UV-vis-NIR reflectance spectroscopy. The results of recycling tests for the three $\text{Fe}^{\text{II}}\text{-R}^{\text{NHC}}\text{@AlF}$ catalysts in CyH oxidation reactions were depicted in Fig. 2. The catalytic activity of $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}\text{@AlF}$ and $\text{Fe}^{\text{II}}\text{-H}^{\text{NHC}}\text{@AlF}$ was gradually decreased with each cycle for catalytic oxidation (Fig. 2a, b). In addition, the UV-vis-NIR reflectance spectra of the two catalysts showed disappearance of absorptions derived from the corresponding Fe^{II} complexes (Figs. S10 and S11 in the ESI). It is noteworthy that the catalytic activity of $\text{Fe}^{\text{II}}\text{-Me}^{\text{NHC}}\text{@AlF}$ retains up to the 5th run (Fig. 2c). The total TONs relate to the amount of Fe complexes based on the UV-reflectance spectroscopy (Fig. S10–S12, Table S5–S7). Thus, decrease of the catalytic reactivity was caused by desorption of Fe complexes in $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}\text{@AlF}$ and $\text{Fe}^{\text{II}}\text{-H}^{\text{NHC}}\text{@AlF}$ from the surface of AlF . The high recyclability of $\text{Fe}^{\text{II}}\text{-Me}^{\text{NHC}}\text{@AlF}$ was derived from the δ property of the methyl groups on the benzimidazole moiety, inducing stronger electrostatic interaction than other complexes; this stronger interaction makes $\text{Fe}^{\text{II}}\text{-Me}^{\text{NHC}}$ stay in the hydrophobic micro-environment of AlF . Furthermore, $\text{Fe}^{\text{II}}\text{-Me}^{\text{NHC}}\text{@AlF}$ catalyst could hold the activity by the 7th run (Fig. S12, Tables S7). Thus, $\text{Fe}^{\text{II}}\text{-Me}^{\text{NHC}}\text{@AlF}$

catalyst has the recyclability, high $2e^-$ -oxidation selectivity and high TON for CyH oxidation reaction in acetonitrile.

Catalytic oxidation of Cyene was also performed using the three heterogeneous catalysts with H_2O_2 in acetonitrile at 313 K under Ar. Products obtained were analysed by GC-MS analysis. The oxidation products derived from cyclohexene were 2-cyclohexen-1-ol (Cyene-OH), 2-cyclohexen-1-one (Cyene=O) and cyclohexene oxide (Cyene-oxide). The TONs obtained for three catalysts with H_2O_2 are listed in Table 2. In the Cyene oxidation, the $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}\text{@AlF}$ catalyst shows highest total TON 908 of all catalysts (Table 2). In contrast, we confirmed that $\text{Fe}^{\text{II}}\text{-R}^{\text{NHC}}$ complexes as homogeneous catalysts and the support $\text{H}^+\text{@AlF}$ showed 100-fold lower catalytic activity and no reactivity in Cyene oxidation with H_2O_2 (Table S8). The high selectivity for epoxidation as reflected in the ratio (Cyene-oxide/(Cyene-OH + Cyene=O)) was observed for the oxidation of Cyene using $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}\text{@AlF}$ as the catalyst. The high selectivity of epoxidation (90%) for $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}\text{@AlF}$ suggests that the electron-withdrawing effect of chloro groups can stabilize the Fe^{II} -hydroperoxo ($\text{Fe}^{\text{II}}\text{-OOH}$) species, which should be responsible for the epoxidation.^{12,13}

Table 2. Catalytic oxidation of cyclohexene by H_2O_2 (30% aq) and $\text{Fe}^{\text{II}}\text{-R}^{\text{NHC}}\text{@AlF}$ in CH_3CN under Ar.

R	Product	TON ^a	Cyene-oxide/ (Cyene-OH + Cyene=O)
Cl	Cyene-oxide	816	8.9
	Cyene-OH	71	
	Cyene=O	21	
H	Cyene-oxide	503	1.6
	Cyene-OH	208	
	Cyene=O	110	
Me	Cyene-oxide	305	2.0
	Cyene-OH	112	
	Cyene=O	42	

^a TONs = [product]/[catalyst]. Conditions: catalysts: 10 nmol, $[\text{H}_2\text{O}_2]$ = 16 mM, [substrate] = 100 mM, T = 313 K, and reaction time = 3 h. TONs were determined by GC-MS spectroscopy. Any side-reaction products except those listed in the table were not observed.

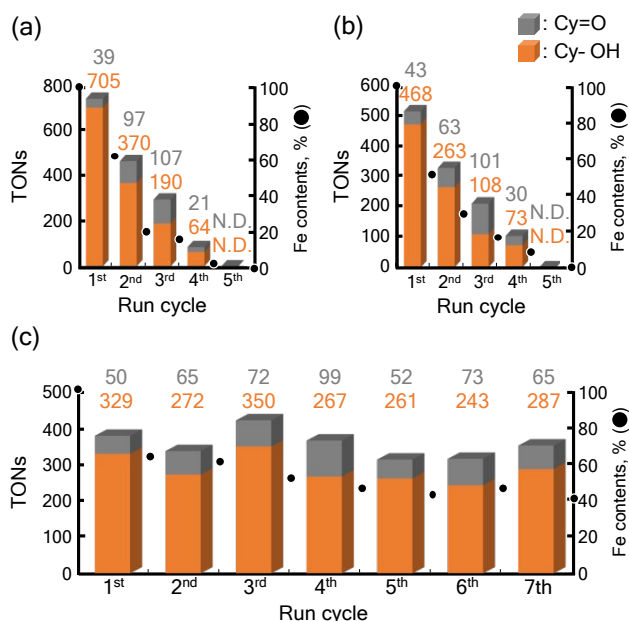


Fig. 2 Total TONs for catalytic CyH oxidation reactions and Fe contents based on the UV-vis-NIR reflectance spectroscopic measurements after each catalytic run using $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}\text{@AlF}$ (a), $\text{Fe}^{\text{II}}\text{-H}^{\text{NHC}}\text{@AlF}$ (b) and $\text{Fe}^{\text{II}}\text{-Me}^{\text{NHC}}\text{@AlF}$ (c) with H_2O_2 . Conditions: catalyst: 10 nmol, $[\text{H}_2\text{O}_2]$ = 16 mM, [substrate] = 100 mM, T = 313 K, and reaction time = 3 h. TONs were determined by GC-MS spectroscopy. Any byproducts were not observed. N.D.: Not detected. Fe contents, % = $(K/M)_x / (K/M)_0 \times 100$ (X = number of catalytic runs). $(K/M)_x$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of catalyst after the X -th catalytic run. $(K/M)_0$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of a catalyst before reaction.

The redox potentials of $\text{Fe}^{\text{II}}\text{-R}^{\text{NHC}}$ complexes in CH_3CN were determined by electrochemical measurements. Each complex showed a reversible redox wave due to the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple at 0.93 V ($R = \text{Me}$), 0.95 V ($R = \text{H}$), and 1.01 V ($R = \text{Cl}$) vs. SCE (Fig. S13 in the ESI). We also measured ESR spectra of reaction mixtures of $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}$ and H_2O_2 in CH_3CN at 77 K, and no ESR signal due to Fe^{III} species (Fig. S14 in the ESI). In addition, the ESI-MS spectrum of the reaction mixture showed a peak cluster assigned to $[\text{Fe}^{\text{II}}(\text{OOH})(\text{Cl}^{\text{NHC}})]^+$ at $m/z = 570.99$ (Fig. S15 in the ESI). The results suggest that electron transfer from $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}$ to H_2O_2 does not occur to form Fe^{III} species, but $\text{Fe}^{\text{II}}\text{-Cl}^{\text{NHC}}$ reacts with H_2O_2 to form the $\text{Fe}^{\text{II}}\text{-OOH}$ intermediate. Based on the results of catalytic reactions for CyH and Cyene oxidation, a plausible reaction mechanism is proposed as shown in Fig. 3. In the first step, an Fe^{II} -acetonitrile complex is converted to the corresponding $\text{Fe}^{\text{II}}\text{-OOH}$ complex through ligand substitution, which is enhanced by strong *trans* effect of the NHC ligand,¹⁴ by H_2O_2 followed by deprotonation. This $\text{Fe}^{\text{II}}\text{-OOH}$ species can react

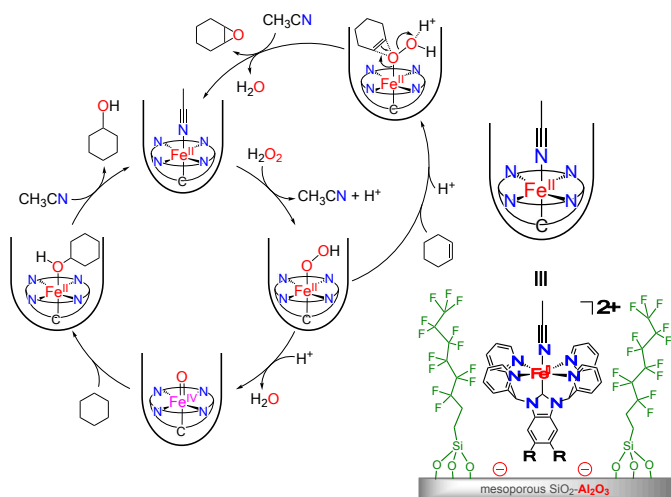


Fig. 3 Proposed mechanisms of the hydroxylation of cyclohexane and epoxidation of cyclohexene by $\text{Fe}^{\text{II}}\text{-NHC@AlF}$ and H_2O_2 .

directly with Cyene to produce Cyene-oxide. As a minor pathway, the $\text{Fe}^{\text{II}}\text{-OOH}$ intermediate undergoes O-O bond heterolysis to afford an $\text{Fe}^{\text{IV}}\text{-oxo}$ ($\text{Fe}^{\text{IV}}\text{=O}$) complex⁶ to perform hydroxylation at the allylic positions *via* hydrogen atom transfer (HAT) to form Cyene-OH, which undergoes overoxidation to afford Cyene=O. In CyH oxidation, the $\text{Fe}^{\text{II}}\text{-OOH}$ species does not react with the substrate and is converted to the $\text{Fe}^{\text{IV}}\text{=O}$ species, which can hydroxylate CyH through HAT.⁸

In conclusion, we have demonstrated catalytic oxidation reactions of CyH and Cyene by H_2O_2 as an oxidant and the immobilized $\text{Fe}^{\text{II}}\text{-NHC}$ catalysts on the hydrophobic fluorinated Al-SBA-15 to afford $2e^-$ -oxidized products, Cy-OH from Cy-H and Cyene-oxide from Cyene, respectively, with high TON and selectivity in acetonitrile in comparison with ever reported Fe-based catalysts (Table S9).^{3a,12,15} This is the first example for the introduction of hydrophobic environment on the aluminosilicate surface as a support of catalysts for the preparation of heterogeneous metal-complex catalysts. This work provides a strategy of introduction of hydrophobic second-coordination sphere to a transition metal complex as a catalyst without time-consuming and tiresome ligand synthesis. The strategy to construct hydrophobic micro-environment around a metal complex as a catalyst will be applied to chemical conversion of various hydrophobic organic compounds in high efficiency and selectivity in polar media.

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Conflicts of interest

There are no conflicts to declare.

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