

A new non-metal heterogeneous catalyst for the activation of hydrogen peroxide: a perfluorinated ketone attached to silica for oxidation of aromatic amines and alkenes

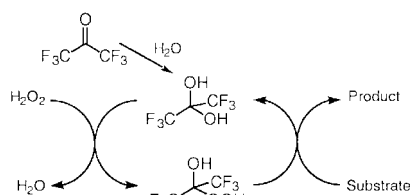
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A silane functionalized by octafluoroacetophenone was polymerized by the sol-gel method to form an insoluble silicate with perfluoroketone pendants; the silicate was used as a heterogeneous catalyst for the activation of aqueous hydrogen peroxide and the oxidation of aromatic amines and alkenes.

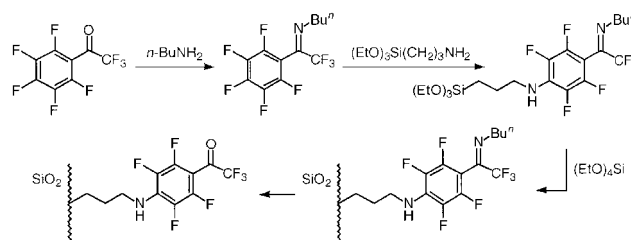
The preparation of heterogeneous catalysts for the activation of hydrogen peroxide and their use for oxidation of organic substrates has been the subject of rather intense research efforts over the last 10–15 years. Almost exclusively this effort has been concentrated on the incorporation of metal-based catalysts onto or into inert matrices. This has been achieved either by substitution of active metals (titanium, vanadium *etc.*) into molecular sieves¹ or amorphous silica,² or by encapsulation or attachment of organometallic catalysts onto supports.³ There are only a few organic compounds capable of activating hydrogen peroxide. Thus, under basic conditions hydrogen peroxide can be used for the epoxidation of electron deficient alkenes⁴ and this has led to guanidine functionalized silica for such reactions.⁵ A perfluorinated ketone, hexafluoroacetone, also is a known compound capable of reacting with hydrogen peroxide to yield an α -hydroperoxyperfluoro alcohol intermediate capable of reacting with nucleophilic substrates to give oxygenated products,⁶ Scheme 1. The high toxicity and volatility of hexafluoroacetone has prevented the wide use of this catalytic system. Recently, a high molecular weight perfluoroketone with less volatility has been suggested as a suitable improvement for hexafluoroacetone in similar oxidation reactions.⁷



Scheme 1

Now we present a silica immobilized perfluoroketone as an effective heterogeneous recyclable catalyst for the oxidation of aromatic amines such as pyridine and its derivatives and aniline and its derivatives in addition to alkenes, using aqueous hydrogen peroxide as oxygen donor. The strategy for the preparation of the perfluoroketone non-metal silicate catalyst is presented in Scheme 2. First, the ketone moiety of octafluoroacetophenone was protected by formation of an imine with *n*-butylamine. The protected perfluoroketone was then attached to an aminosilane by nucleophilic substitution and the insoluble silicate was prepared by co-polymerization with tetraethoxysilane by the sol-gel method. The final heterogeneous catalyst was then obtained by removal of the *n*-butylamine protecting group.[†]

The perfluoroketone-silicate catalyst was tested for activity with several substrate types.[‡] First, the oxidation of pyridine



Scheme 2

and derivatives to the corresponding *N*-oxides, showed that the catalyst was quite effective for this reaction, Table 1. The yields were generally high for some representative substrates such as pyridine, 2- and 4-methylpyridine, quinoline, and 4-methylquinoline; *N*-oxides were the only products. Interestingly, 8-hydroxyquinoline was less reactive, presumably because of steric considerations, and the electron-poor 2,6-dichloropyridine was unreactive as expected. The oxidation of aniline and its derivatives catalysed by the perfluoroketone-silicate gave somewhat more surprising results, Table 2. Aniline, alkyl-

Table 1 Oxidation of pyridine derivatives with 60% H₂O₂ catalysed by the perfluoroketone-silicate

Substrate	Product	Yield (mol%)
Pyridine	Pyridine 1-oxide	99
2-Methylpyridine	2-Methylpyridine 1-oxide	84
4-Methylpyridine	4-Methylpyridine 1-oxide	93
Quinoline	Quinoline 1-oxide	87
4-Methylquinoline	4-Methylquinoline 1-oxide	83
8-Hydroxyquinoline	8-Hydroxyquinoline 1-oxide	20
2,6-Dichloropyridine	2,6-Dichloropyridine 1-oxide	0

Reaction conditions: 0.8 mmol substrate, 20 mg (0.05 mmol ketone) perfluoro-silicate, 1 mL acetonitrile, 3 mmol 60% H₂O₂, 24 h, 80 °C. Yields were computed by GC analysis.

Table 2 Oxidation of aniline derivatives with 60% H₂O₂ catalysed by the perfluoroketone-silicate

Substrate	Product	Yield (mol%)
Aniline	Diphenyldiazene 1-oxide	100
3-Methylaniline	Bis(3-methylphenyl)diazene 1-oxide	100
2-Ethylaniline	Bis(2-ethylphenyl)diazene 1-oxide	100
3-Trifluoromethylaniline	Bis(3-trifluorophenyl)diazene 1-oxide	100
3-Fluoroaniline	Bis(3-Fluorophenyl)diazene 1-oxide	100
3-Nitroaniline	1,3-Dinitrobenzene	100
2-Methyl-4-hydroxyaniline	4-Nitro-5-methylphenol	100
4-Hydroxyaniline	4-Nitrophenol	100
2-Nitroaniline	None	—
4-methoxy-2-nitroaniline	None	—

Reaction conditions: 0.8 mmol substrate, 20 mg (0.05 mmol ketone) perfluoro-silicate, 1 mL acetonitrile, 3 mmol 60% H₂O₂, 12 h, 80 °C. Yields were computed by GC analysis.

substituted aniline and halogen-substituted aniline derivatives all yielded the dimeric azoxy compounds as *sole* products in quantitative yields. On the other hand aniline with electron donating hydroxy substitution or electron withdrawing nitro substitution yielded the corresponding nitro derivatives, provided the nitro was not *ortho* to the amino substituent. In this latter case there was no reaction, possibly related to intramolecular hydrogen bonding between the amino and nitro substituents. For the other cases, we have as yet no satisfactory explanation for partial oxidation and the *selective* formation of azoxy compounds on the one hand for aniline, alkylated anilines and halogenated anilines and full oxidation to nitro derivatives in the case of 3-nitroaniline and 4-hydroxyaniline.

The catalytic activity of the perfluoroketone–silicate was also tested for oxidation of alkenes, Table 3. For less nucleophilic substrates such as oct-1-ene and oct-2-ene, activity was low although the initial epoxide product formed was stable under the reaction conditions and epoxides were obtained selectively. More nucleophilic substrates such cyclohexene, 1-methylcyclohexene and 2,3-dimethylbut-2-ene were much more reactive and high conversions were obtained. However, selectivity to the epoxide was very low due presumably to acid catalysed formation of diols or pinacol rearrangement. Interestingly, primary allylic alcohols reacted to yield mostly aldehyde as the product using 30% H₂O₂; no epoxidation was observed. Thus, 0.8 mmol (*Z*)-hex-2-en-1-ol was reacted with 2 mmol 30% H₂O₂ in 1 mL EtOAc at 80 °C for 24 h to yield 94% hex-2-enal.

Finally, the stability and activity of the catalyst was tested in a multi-recycle experiment. Thus, 4 mmol aniline, 100 mg

Table 3 Oxidation of alkenes with 60% H₂O₂ catalysed by the perfluoroketone–silicate

Substrate	Products (Yield (mol%))	Conversion (mol%)
Cyclooctene	Cyclooctene oxide (100)	78
Oct-2-ene	Oct-2-ene oxide (100)	16
Oct-1-ene	Oct-1-ene oxide (100)	6
Cyclohexene	Cyclohexane-1,2-diol (80) Cyclohex-2-en-1-ol (15) Other (5)	61
1-Methylcyclohexene	1-Methylcyclohexane-1,2-diol (86) 2-Methylcyclohexanone (10) Other (4)	100
2,3-Dimethylbut-2-ene	2,3-Dimethylbut-2-ene oxide (16) 2,3-Dimethylbutane-2,3-diol (21) 2,3-Dimethylbutan-2-one (63)	100

Reaction conditions: 0.8 mmol substrate, 20 mg (0.05 mmol ketone) perfluoro–silicate, 1 mL acetonitrile, 3 mmol 60% H₂O₂, 24 h, 80 °C. Yields were computed by GC analysis.

(0.25 mmol ketone) perfluoro–silicate and 15 mmol 60% H₂O₂ were mixed in 5 mL acetonitrile at 80 °C for 18 h. More than 98% of the aniline reacted to diphenyldiazene 1-oxide. The mixture was filtered and the catalyst washed twice with dichloromethane, dried and reused in an additional reaction. Over a period of five reaction cycles, as described above, no significant loss of activity was observed and yields of diphenyldiazene 1-oxide remained >95%.

Notes and references

† Octafluoroacetophenone (6 mmol, 1 g) was reacted with *n*-butylamine (6 mmol, 0.57 mL) in 50 mL dry toluene for 5 h at 60 °C in a 250 mL flask. After this time 3-aminopropyl(trimethoxy)silane (6 mmol, 1.43 mL) was added and the solution was heated and stirred under reflux while the reaction was monitored by ¹⁹F NMR (CDCl₃). The starting compound (Shiff base) has peaks at –75.7 ppm (s, β position, 3F), –161.6 ppm (d, *ortho* position, 2F), –138.2 ppm (m, *meta* position, 2F) and –153.2 ppm (d, *para* position, 1F), whereas the product has peaks at –75.7 ppm (s, β position, 3F), –160.3 ppm (d, *ortho* position, 2F) and –141.5 ppm (m, *meta* position, 2F). After one week the reaction was complete and tetraethoxysilane (9 mmol, 2 mL), water (3 mL), dibutyltin dilaurate (0.09 mL, 0.15 mmol) in 100 mL of ethanol were added; the solution was then heated at 60 °C for 12 h. After this time, the reaction mixture was transferred into a beaker and the solvent(s) was allowed to evaporate at rt until a yellow–brown solid was obtained. After grinding the silicate to a coarse powder, the solid was treated by Soxhlet extraction with diethyl ether followed by dichloromethane. The silicate was then treated with 100 mL 30% H₂O₂ under reflux for 16 h to remove the protecting group (verified by IR spectroscopy—carbonyl peak at 1640 cm^{–1}). The white powder that was obtained was filtered and washed consecutively by water, acetonitrile and finally with dichloromethane. After drying under vacuum at 60 °C overnight, the silicate was used in the catalytic studies.

‡ The reaction ingredients as noted in the tables were placed in 5 mL vials; the vials were closed and placed in an oil bath at 80 ± 2 °C and the contents stirred magnetically for the noted time period. After the reaction was completed the organic phase was extracted with dichloromethane (5 mL) and analyzed by GC and GC-MS using a 30 m 5% phenylmethylsilicone capillary column (0.32 mm id, 0.25 μm coating).

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