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Oxidative organic transformations catalysed by titanium silicate molecular sieves

PRADEEP KUMAR, RAJIV KUMAR[+] AND BIPIN PANDEY[*]
Division of Organic Chemistry: Technology, [+]Catalysis Division, National Chemical Laboratory, Pune 411 008, India.

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Abstract

Titanium silicate molecular sieves, TS-1 and TS-2, are found to catalyse a variety of oxidation reactions in the presence of dilute H_2O_2 as oxidant. The reactions reported are the hydroxylation of aromatic compounds, oxidation of alcohols, the oxyfunctionalisation of alkanes, the epoxidation of alkenes and allyl alcohols, the cleavage of carbon–carbon or carbon–nitrogen double bonds, the oxidation of amines, the ammoximation of carbonyl compounds, the oxidation of cyclic dienes and sulfides. The plausible mechanism involving the reactive species, *e.g.*, peroxytitanium complexes for the above reactions is described.

Key words : Zeolite, molecular sieves, oxidation, TS-1/TS-2, hydroxylation, oxyfunctionalisation, epoxidation, ammoximation, sulfoxidation.

1. Introduction

Zeolites are endowed with unique physical and chemical characteristics which offer opportunities to manipulate active site microenvironment. Indeed, a recent account[1] compares this ability of zeolites with catalytic antibodies[2] and metalloenzymes[3]. Some of the prominent physical characteristics of zeolites are its ruggedness to temperature and pressure and its ability to recognise, discriminate and organise molecules with less than an angstrom-level precision at the active sites, whereas the noteworthy chemical characteristics are the possibilities of manipulating framework metal ion properties, *e.g.*, acidic and basic (either Lewis or Brönsted), oxidising and reducing, etc[4–6]. Naturally, such advantages have led to significant applications in heterogeneous catalysis, separation technology, optoelectronics and chemical sensing[4–6]. The commerical success of zeolites is mainly due to the continued discovery of new materials that have enabled process improvements and development of new technologies.

One of the latest arrivals on the zeolite scene is crystalline microporous titanium silicate molecular sieves, TS-1[7] and TS-2[8] where Ti^{4+} ions are incorporated in MFI and MEL frameworks, respectively. The advent of these non-acidic microporous titanium silicate

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[*] For correspondence.
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molecular sieves (TS-1 and TS-2) has given an impetus to the catalytic oxidation of various organic compounds. The pore architecture of TS-1 (MFI group) consists of ten-membered rings intersecting straight and zig-zag channels with pore openings of 0.51×0.55 nm (straight channels) and 0.54×0.56 nm (zig-zag channels). However, TS-2 (MEL topology) is composed of ten-membered ring straight channels of 0.54×0.56 nm pore openings.

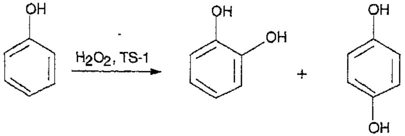
2. Synthesis of titanium silicate molecular sieves

The details about synthesis and characterisation of TS-1[9,10] and TS-2[8,11] have been reported in the literature. Titanium silicate molecular sieve TS-1/TS-2 can generally be synthesized by mixing tetraethylorthosilicate, tetrabutylorthotitanate and tetrapropylammonium hydroxide (in the case of TS-1) or tetrabutylammonium hydroxide (in the case of TS-2) and autoclaving the final clear mixture at 443K for 2–3 days. The crystalline materials were filtered, washed, dried and calcined at 823K for 16 h in dry air. The calcined form of titanium silicate was treated twice with 1N ammonium acetate and calcined at 773K for 6 h before use in the reaction.

3. Hydroxylation of aromatic compounds

The direct hydroxylation of aromatic hydrocarbons to phenol or phenol derivatives can be carried out by means of H_2O_2 and TS-1[12]. The oxidation of phenol[13] with dilute H_2O_2 in the presence of TS-1 catalyst gives hydroquinone and catechol in almost equal ratio. The selectivity of H_2O_2 towards hydroxy products was found to be 80–85%. This process has already been employed industrially on large scale, (100,000 t/a) in Italy. The direct aromatic hydroxylation of benzene[14] and substituted benzene[15] such as toluene, ethylbenzene, anisole and cresol is also possible by the use of the H_2O_2/TS-1 system. The hydroxylation of aromatic hydrocarbons by dilute H_2O_2 also takes place over TS-2. The reactivity of TS-2 is similar to that of TS-1. Benzene and monsubstituted benzenes like phenol, toluene, etc., undergo hydroxylation rapidly, while compounds containing electron-withdrawing groups do not react so easily. Similarly, the reaction of compounds with bulky groups like *t*-butyl is also not easy due to the steric restriction imposed by the pore size of zeolite. The oxidation reaction is faster with aromatic compounds containing electron-donating substituents. Like electrophilic substitution, *o*- and *p*- products are found to predominate. TS-2/H_2O_2 system catalyses the oxidation of benzene to phenol which can further be hydroxylated to yield the dihydroxybenzenes.

The exact mechanism of aromatic hydroxylation with H_2O_2 is not yet known. However, the reactivity profile of aromatics, *i.e.*, electron-donating substitutions enhance the reactivity towards TS-1/H_2O_2, does indicate that the nature of active species is electrophilic in nature. For further discussion on the nature of active species, see the mechanistic discussion in the following sections.



SCHEME 1.

4. Oxidation of alcohols

Primary and secondary alcohols are oxidised to aldehydes and ketones, respectively, by H_2O_2 in the presence of TS-1 catalyst. This offers a new and efficient heterogeneous catalytic route for the synthesis of carbonyl compounds[16]. Thus, benzyl alcohol can be oxidised to benzaldehyde by H_2O_2 in approximately 90% yield (based on H_2O_2 conversion) over TS-1 at 70–90°C. The obvious side reaction is the formation of acetals and further oxidation into carboxylic acid in the above transformation. Secondary alcohols are oxidised to ketones by the application of H_2O_2/TS-1 combination. 2-Butanol can be oxidised 1.2 times faster than 2-pentanol[17]. More interestingly, 2-pentanol reacted 13 times faster than 3-pentanol. These observations clearly indicate that the shape-selective nature of zeolite plays an important role during oxidation reaction.

$$C_6H_5CH_2OH \xrightarrow{H_2O_2,\ TS\text{-}1} C_6H_5CHO$$

SCHEME 2.

5. Oxyfunctionalisation

5.1. *Alkane oxidation*

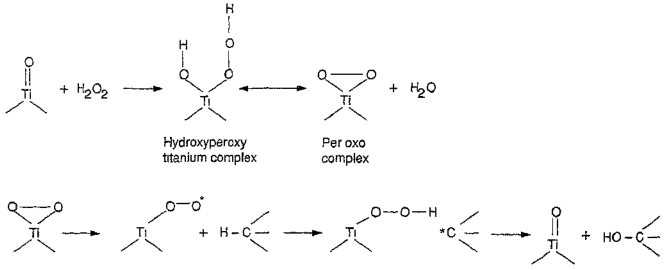
Because of the chemical inertness of alkane, the introduction of oxygen in alkanes proceeds with low selectivities over most homogeneous and heterogeneous catalysts[18,19]. However, recently it has been shown[20,21] that TS-1 can efficiently catalyse the oxidation of alkane by H_2O_2. The titanium silicate can activate secondary and tertiary carbon atoms in alkanes with consecutive oxidation to alcohols and then to ketones using aqueous H_2O_2. Huybrechts *et al*[20] have found that the oxidation occurs selectively at the tertiary C–H in the oxyfunctionlisation of hexane, 2-pentane and 2-methylpentane. The oxidation of primary C–H bonds could not be detected. The reactivity order for alkane functionalisation is as follows: tertiary C–H > secondary C–H. Subsequently, results from our laboratory[22] have shown that the TS-2 can also catalyse the oxidation of alkanes with high selectivities. The major products in the oxidation reaction of *n*-hexane are found to be 2- and 3-hexanols and 2- and 3-hexanones. The oxidation of *n*-hexane over different zeolites with MEL structure, *e.g.*, TS-2, Al-TS-2, ZSM-11, silicalite-2, SiO_2 was studied. The most active catalyst was found to be TS-2. These results show that Ti^{4+} ions are the active sites which are responsible for the selective oxidation of alkanes. Like TS-1, TS-2 also activates the 2- and 3-position to a large extent for the insertion of oxygen function. This observation is in full agreement with the results reported by Huybrechts *et al*[20] in their studies for oxidation employing TS-1 as catalyst. The results of selective oxidation carried out on a number of other alkanes using TS-2 as catalyst[23] reveal that conversion decreases with increasing carbon number. This could be attributed to the slower diffusion of the larger molecules into zeolite channels. The relevance of diffusion concept has been further substantiated from the observation that when equimolar mixtures of *n*-hexane +3 methyl pentane, *n*-hexane + 2,2-dimethylbutane and *n*-hexane + cyclohexane are allowed to react simultaneously in the presence of TS-2 catalyst, the faster diffusing *n*-hexane undergoes reaction preferentially.

5.2. *Selective oxidation of cyclohexane*

Among alkane oxidations, the conversion of cyclohexane to cyclohexanone *via* cyclohexanol also constitutes an important reaction of industrial significance. The reaction with transition metal catalysts proceeds with low conversion and poor selectivities[24] whereas TS-2/H_2O_2 combination works efficiently for this reaction. The results from our laboratory[25] show that an increase in the reaction temperature increases the conversion of cyclohexane and favours the formation of cyclohexanone. For example, the cyclohexanone to cyclohexanol mole ratio is 0.45 at 353K, while it is 1.30 at 393K. The mole proportion of H_2O_2 also influences the product distribution. For example, the cyclohexanone/cyclohexanol ratios are 1.0 and 0.5 when H_2O_2; cyclohexane are used in 1.0 and 0.2 molar ratios.

5.3. Nature of reactive species

Insight regarding the nature of reactive species in the oxidation of alkanes over TS-1 has been proposed by Huybrechts *et al*[20] as depicted in Scheme 3.



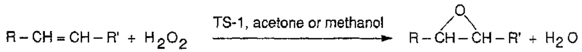
SCHEME 3. Oxidation of alkane over TS-1.

According to the proposed mechanism the > Ti=O group, believed to be an active site in zeolite framework, reacts with H_2O_2 to give peroxy species *via* an intermediate hydroxyperoxytitanium complex, which eventually provides the reactive electrophilic oxygen species for the oxidation of alkane. The >Ti=O (surface titanyl) group has been shown[7,26] to possess an infrared band at 960 cm^{-1}, which, on reaction with H_2O_2, disappears and a new absorption band at 425 nm in visible region appears which is characteristic of peroxotitanium complex[27]. Presumably, the oxidation of alkane involves diradical intermediate followed by hydrogen abstraction from the alkane to give a carbon radical. Recombination with the hydroxyl radical from Ti–O–OH yields the alcohol and the titanyl group.

6. Epoxidation

TS-1 has been found to catalyse the epoxidation reaction of various olefins and diolefins with almost 100% H_2O_2 conversion and selectivities of 75–96% (based on olefin)[28-32].

Propylene can be oxidised to the industrially important compound propylene oxide in the presence of TS-1 using hydrogen peroxide as an oxidising agent[28,32]. In acetone at 40°C, propylene oxide is obtained with 93% selectivity at 94% H_2O_2 conversion. Kumar *et al*[33] have recently studied the epoxidation of styrene by TS-1/H_2O_2 system. The major reaction was the formation of epoxide and its efficient isomerisation into phenylacetaldehyde. The byproduct was benzaldehyde formed due to the cleavage of C=C. Protic and aprotic solvents have marked influence on the product distribution. In acetone, phenylacetaldehyde selectivity was very high, while in methanol, apart from the formation of phenylacetaldehyde, alcoholysis (addition of methanol to epoxide) occurred to a large extent forming 2-methoxy-2-phenyl-ethanol (sel. 40%). Thus, this synthetic route offers an alternative and improved process for the oxidation of olefinic organic compounds. The additional features of the process are that it operates at relatively low temperature and is environmentally friendly and safe.



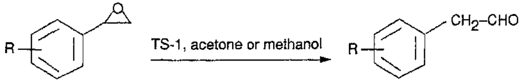
$$R-CH=CH-R' + H_2O_2 \xrightarrow{\text{TS-1, acetone or methanol}} R-\overset{O}{\overbrace{CH-CH}}-R' + H_2O$$

R, R' = H, alkyl, aryl, alkylaryl, cycloalkyl

SCHEME 4.

6.1. *Rearrangement of epoxides*

Epoxides are known to undergo ring opening reaction by Lewis and Brönsted acid catalysts. Heterogeneous catalysts such as titanium silicate molecular sieve (TS-1) catalyse the epoxide opening into aldehyde in liquid phase which can be visualised as a secondary reaction during epoxidation. As shown in the following scheme, the styrene oxide or alkyl or alkoxy-substituted styrene oxides undergo isomerisation over TS-1 in acetone or methanol at 30–100°C to give phenylacetaldehyde with > 75–90% selectivities and at conversion between 90 and 100%[33,34]. The TS-1-induced high regioselective conversion of styrene oxides into phenyl acetaldehyde may be attributed to the stabilization of the benzyl cation by the adjacent phenyl ring[4].



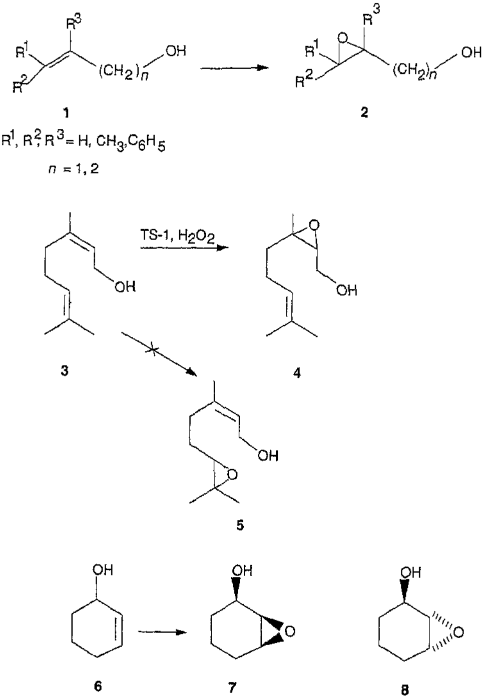
R = alkyl, aryl, arylalkyl, halogen, haloalkyl, alkoxy, alkylthio

SCHEME 5.

6.2. *Epoxidation of unsaturated alcohols*

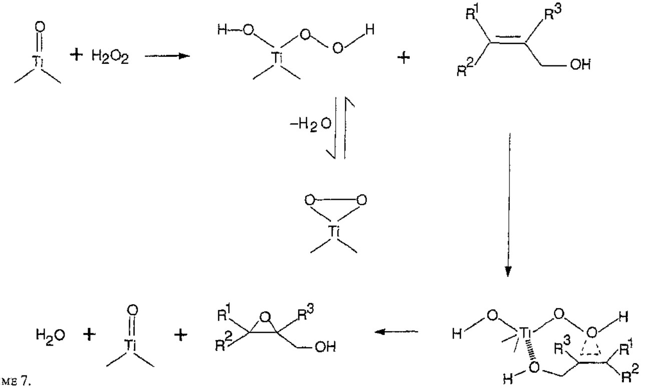
Recently, Tatsumi *et al*[35] have reported that TS-1 can catalyse the epoxidation of allylic alcohols which is dependent on the structure of unsaturated alcohol. With unsaturated alcohols having an internal –CH = CH– double bond, epoxidation of the double bond and the oxidation of alcohol to the aldehyde or ketone occurred competitively. Epoxidation of a terminal

$CH_2{=}CH-$ double bond in unsaturated alcohol was found to be slow, compared to that of the internal double bond. Further, recent findings from our group[36] show that hydroxyl group assists chemoselective epoxidation of allylic alcohols in moderate to good yields using TS-1 and dilute (30%) H_2O_2. As shown in Scheme 6, geraniol undergoes chemoselective epoxidation by TS-1/H_2O_2 system in 80% yield with 86% conversion. The nature of reactivity pattern in this reaction clearly indicates that OH does assist epoxidation. Additionally, our studies reveal that hydroxyl-assisted epoxidation using TS-1/H_2O_2 combination is stereospecific and stereoselective as well. Thus, cyclohexenol **6** gave **7** as major product, where epoxide and OH are *cis* to each other and **8** as minor product, where epoxide and OH are *trans* to each other. This development is valuable in planning of Ti-containing zeolite-based asymmetric epoxidation.



SCHEME 6.

A plausible catalytic cyclic mechanism which accounts for the efficient hydroxyl-assisted chemoselective epoxidation is shown in the following scheme. Some of the reactive species, *e.g.*, hydroxyperoxy, peroxy complexes in the presence of H_2O_2 are routinely being proposed for oxidation processes involving TS-1[20]. Presumably, the enhanced reactivity of OH-containing olefins and OH-assisted chemoselectivity is due to the formation of a species from allylic alcohol and hydroxyperoxytitanium complexes as depicted in Scheme 7.



SCHEME 7.

7. Carbon–carbon double bond (C=C) cleavage

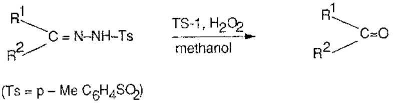
Recently, it has been reported[37] that various zeolites including both TS-1 and TS-2 could be used as catalysts for the cleavage of carbon–carbon double bond of various alkanes in the presence of aqueous H_2O_2 as an oxidant. In the conversion of α-methylstyrene into acetophenone over titaniumsilicate molecular sieves, the overall selectivity was found to be quite high (66 and 48% over TS-2 and TS-1, respectively) towards C=C bond cleavage. The other products were corresponding epoxide, aldehyde and diol. TS-2 exhibited slightly better selectivity for C=C cleavage than TS-1.

8. Carbon–nitrogen double bond (C=N) cleavage

Titanium silicate molecular sieves not only catalyse the oxidation of carbon–carbon double bond, but can be successfully employed for the cleavage of carbon–nitogen double bond as well. Recently, we have shown that TS-1 can catalyse the oxidative cleavage of various tosylhydrazones and imines to their corresponding carbonyl compounds in the presence of dilute H_2O_2 (30%) as an oxidant[38].

The reaction works particularly well for the tosylhydrazones of ketones with almost quantitative conversion and excellent yield of the product but with aldehyde; further oxidation to carboxylic acid and subsequent reaction with solvent methanol to give ester was observed.

Mechanistically, the cleavage of carbon–nitrogen double bond involved an electrophile as an active species, which is present in hydroxyperoxo or peroxo species as discussed earlier

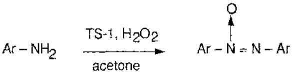


SCHEME 8.

for most of the oxidative transformation with TS-1/H_2O_2. The electrophilic oxygen species brings the oxidation of imino double bond of tosylhydrazones or Schiff base to oxaziridine derivatives. Subsequent oxidative H-abstraction by peroxo or hydroxyperoxo species, radical H-abstraction by OH* or by usual fragmentation due to instability of oxaziridine led to the carbonyl compound.

9. Oxidation of amines

Recent findings from our laboratory have shown that TS-1/H_2O_2 combination exhibits a remarkable activity and selectivity in the liquid phase oxidation of aniline to symmetrical azoxybenzene[39].



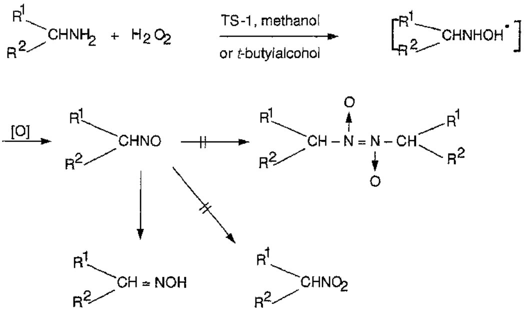
SCHEME 9

In the oxidation of aniline into azoxybenzene over titanium silicate molecular sieves, the conversion with TS-1 was better than TS-2. The yield of azoxybenzene with TS-1 was found to be 87.8% (based on starting material aniline consumed, 9.2% unreacted) whereas the yield of the product with TS-2 catalyst was 64.2% (based on aniline consumed; 29.2% unreacted aniline). In the case of 4-methoxy aniline, the yield was rather low (10%) owing to the formation of many unknown side products. It may be mentioned that there are some naturally occurring azoxybenzene-possessing potent biological properties[40]. Also, metal-catalysed oxidation of amines is of interest because of its relevance to the enzymatic degradation of nitrogen-containing compounds in biological systems[41]. Their utility in liquid crystals is also well known[42].

As discussed earlier, the mechanism of this reaction is believed to involve similar peroxo species generated *in situ* on reaction of silica-bound titanyl (>Ti=O) active site with H_2O_2 which eventually provides the reactive O* species for the oxidation.

Recently, Reddy *et al*[43] have reported that primary aliphatic amines with α-hydrogen atom can be oxidised over titanium silicate molecular sieves in the presence of hydrogen peroxide as oxidant to give the corresponding oximes as the main product. TS-1 catalyses the oxidation of *n*-alkylamine with selective formation of the oxime due to constrained environment of the 10-membered ring, suppressing the formation of the bulky nitroso dimer. As shown in

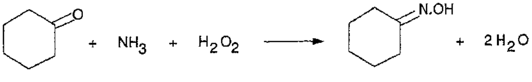
Scheme 10, oxidation of primary aliphatic amine follows consecutive steps with the formation of a number of oxidation products. The activity, oxime selectivity and peroxide efficiency gradually decreases when the alkyl chain length increases, attributing to the shape-selective nature of zeolite. The byproducts in this reaction are alkylazo compound and isomeric hydrazones. Low activity and selectivity were observed with cyclohexylamine. The mechanism of this reaction is assumed to involve peroxo species, which inserts an oxygen atom into the amine giving an alkyl hydroxylamine. The latter is then oxidised to an unstable alkyldihydroxyamine which upon dehydration gives the corresponding nitroso alkane. The latter then rearranges *via* a prototropic shift giving the corresponding oxime. TS-1-catalysed oxidation of secondary amine into the corresponding hydroxylamines has also been reported[44].



SCHEME 10.

10. Ammoximation of carbonyl compounds

Recently, titanium silicate molecular sieve has been found to efficiently catalyse the conversion of cyclohexanone into oxime in the presence of ammonia and H_2O_2 with high selectivities[45,46]. Classical methods employed in the manufacture of cyclohexanone oxime are associated with the coproduction of ammonium sulphate and the use of hazardous chemicals like oleum, halides and oxides of nitrogen. This method offers an environmentally friendly alternative route to cyclohexanone oxime, an intermediate in the manufacture of Nylon-6.



SCHEME 11.

It has been demonstrated that ketoxime can be manufactured by one-pot reaction starting from a secondary alcohol in the presence of O_2, H_2O_2 and ammonia using TS-1 catalyst[47]. For example, cyclohexanol is converted to cyclohexanone oxime at about 100°C in 90% yield.

The ammoximation of cyclohexanone and other carbonyl compounds over TS-2 has recently been reported[48]. Cyclohexanone oxime is obtained in 80.2% yield with 95% selectivity at 84.5% conversion. Similarly, the ammoximation of a number of other carbonyl compounds was also carried out. Thus, benzaldehyde gives 96% of oxime with 96% selectivity and at 100% conversion. Acetophenone oxime is obtained in 53.3% yield with 98.2% selectivity and at 54.3% conversion. 2-Butanone gives 83.5% oxime with 98.2% selectivity at 85% conversion. Benzophenone oxime is obtained in 0.2% yield with 50% selectivity and at 0.4% conversion. Thus, the activity of these compounds followed the decreasing order: benzaldehyde > 2-butanone > cyclohexanone > acetophenone> benzophenone. The higher activity of benzaldehyde could be attributed to its more reactive carbonyl group. The low activity of benzophenone could be due to steric effects, inductive effects and its bulkiness causing difficulty in diffusing into zeolite channels.

Mechanism for ammoximation is believed to involve peroxotitanium complex as indicated in earlier section. There are two plausible mechanisms, 1 and 2, as depicted in Scheme 12. Mechanism 1 involves the catalytic formation of hydroxyl amine which reacts with the carbonyl compound to form the corresponding oxime. Mechanism 2, where an imine formation is involved, appears to be unlikely, mainly because when pure imines were oxidised by TS-1/H_2O_2 system, no oxime was formed and the cleavage of C=N was observed with the formation of corresponding carbonyl compound[38] as discussed in Section 8.

Recently, Ravindranathan *et al*[49] have developed a cost-effective technology for cyclopropyl amine from cyclopropyl methyl ketone involving some of the chemistry discussed above.

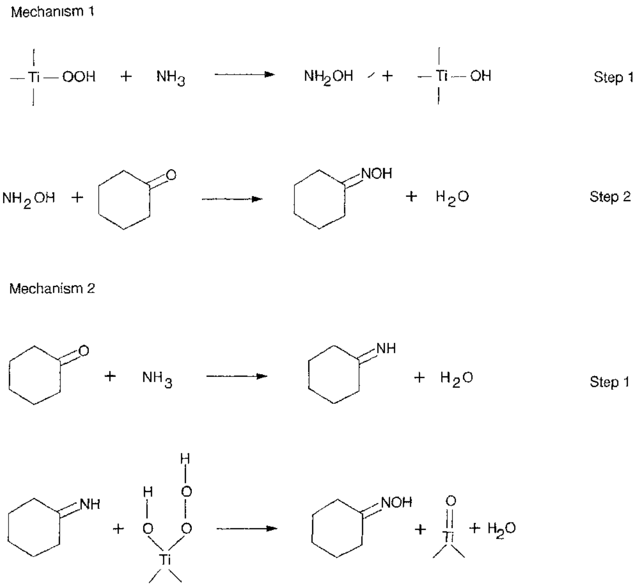
11. Oxidation of cyclic dienes

Another noteworthy reaction which can be carried out on titanium zeolite is the oxidation of cyclic dienes. Thus. recent findings from our group show that when diene, *e.g.*, cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene or furan is treated with aqueous hydrogen peroxide in acetone at reflux temperature in the presence of TS-1, the corresponding hydroxy ketone or lactone is obtained in moderate to good yield[50].

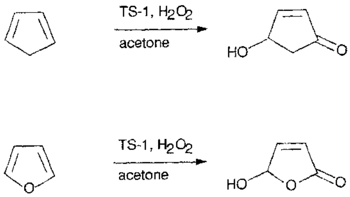
Regarding possible mechanism, as discussed in preceding section, some of the reactive species, *e.g.*, hydroxyperoxy, peroxy in the presence of H_2O_2 are routinely being proposed for oxidation processes involving TS-1. Alternatively, one could invoke the intermediacy of singlet oxygen in the above transformation from diene. The generation of singlet oxygen could be visualised from hydroperoxo or peroxo titanium species. Indeed, when the endoperoxide of CPD was treated under TS-1 conditions, the same product was obtained indicating the intermediacy of $^1O_2$ in TS-1/H_2O_2 chemistry.

12. Sulfoxidation of thioethers

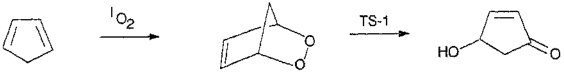
As discussed in the preceding sections, titanium silicate molecular sieves facilitate the catalytic oxyfunctionalisation of carbon moieties in various organic molecules and oxidation of amines. Recently, we have found that these catalysts can also catalyse the oxidation of various thioethers to the corresponding sulfoxides and sulfones using dilute H_2O_2 as an oxidant[51,52].



SCHEME 12.

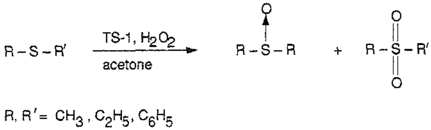


SCHEME 13.



SCHEME 14.

In the oxidation of sulfides with H_2O_2 over TS-2 molecular sieve catalyst, the reactivity of the sulfide followed the order $Me_2S \gg Et_2S > PhSMe > PhSEt$.



SCHEME 15.

We have observed[53,54] that dithiolanes or dithianes can also be oxidised to the sulfoxides and sulphones using titanium silicate molecular sieve in the presence of dilute H_2O_2.

As discussed in the earlier section, the mechanism of this reaction is believed to involve the peroxotitanium complexes as reactive species which eventually provides O^* species required for oxidation. The involvement of singlet oxygen and superoxide has already been established in S-oxide formation in some other studies from our group[55,56].

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