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Selective oxidation of secondary amines over titanium silicalite molecular sieves, TS-1 and TS-2

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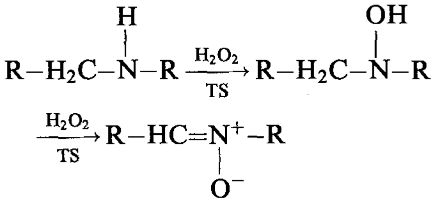
Titanium silicalite molecular sieves, TS-1 and TS-2 having MFI and MEL structures, respectively, catalyze the oxidation of secondary amines to the corresponding hydroxylamines using hydrogen peroxide as the oxidant. Higher concentrations of H_2O_2 lead to further oxidation of hydroxylamine to nitrone. Diffuse reflectance spectroscopy shows the formation of a titanium peroxo complex upon addition of hydrogen peroxide to the TS-1 catalyst. The titanium peroxo complex oxidizes the substrate and reforms to a titanyl group.

Keywords: titanium silicalites; oxidation; amines; hydrogen peroxide

1. Introduction

N,N′-dialkyl hydroxylamines are valuable intermediates as reducing agents and polymerization inhibitors. They are speculated to replace hydrazine derivatives as deoxygenating agents for water. They are also used in the preparation of nitrones, either by condensation with aldehydes or ketones or by direct oxidation [1]. In these methods the major problem is associated with the preparation of hydroxylamines. Oxidation of secondary amines to the corresponding hydroxylamines is known to take place in the presence of hydrogen peroxide [2]. Catalysts containing Mo and W have also been used [3]. However, in all these cases the selectivity for hydroxylamine has been low. Oxidation of carbon atoms and the decomposition of hydrogen peroxide predominate over the oxidation to hydroxylamine. The incorporation of Ti^{4+} in the frameworks of silicalite-1 (TS-1; MFI structure) and silicalite-2 (TS-2; MEL structure) leads to very interesting catalytic properties in various oxidation reactions [4]. Recently, titanium silicalite molecular sieve, TS-1, has been found to catalyze the oxidation of secondary [5] and primary amines [6]. Though, the patent literature claims the oxidation of secondary amines to the corresponding hydroxylamines over the TS-1 catalyst [5], there is no open literature existing on this subject. To avoid the problems involved in the synthesis of hydroxylamines from secondary amines, direct methods for the oxidation of secondary amines to nitrones have also been developed over tungstate [7] and selenium dioxide [8] using hydrogen peroxide. Flavin monooxygenase [9] and model compounds, such as 5-ethyl-4a-hydroperoxyflavin [10] are also known to oxidize secondary amines to nitrones via hydroxylamines. This reaction is not known over titanium silicalite molecular sieves. In this paper, we now report the oxidation of secondary amines to the corresponding hydroxylamines subsequently to nitrones over microporous titanium silicalite molecular sieves in presence of hydrogen peroxide:



$$R{-}H_2C{-}\overset{H}{\overset{|}{N}}{-}R \xrightarrow[TS]{H_2O_2} R{-}H_2C{-}\overset{OH}{\overset{|}{N}}{-}R \xrightarrow[TS]{H_2O_2} R{-}HC{=}\underset{O^-}{\underset{|}{N^+}}{-}R$$

2. Experimental

TS-1 and TS-2 catalysts are prepared according to the reported literature data [11,12]. Before catalytic testing, both catalysts were thoroughly characterized using XRD, framework IR, UV-Vis and chemical analysis. The Si/Ti ratio of TS-1 and TS-2 was 44 and 40, respectively. Catalytic experiments were carried out batchwise. In a typical reaction, catalyst, amine and solvent are stirred in a 100 ml round bottom flask. When the reaction temperature (338 K) is attained, hydrogen peroxide (35 wt% solution) was added dropwise using a syringe. Products collected after 1 h of the reaction are analyzed by an on-column gas chromatograph (50 m CPSil5B column from Chromopack with 0.32 mm internal diameter). Products are identified using GCMS.

3. Results and discussion

The results obtained in the oxidation of diethylamine over TS-1, TS-2 and SiO_2–TiO_2 catalysts are reported in table 1. Table 1 also reports the influence of the nature

Table 1
Influence of nature of the catalyst and the solvent in the oxidation of diethylamine [a]

Catalyst	Solvent	DEA conv. (%)	Hydroxylamine sel. (%)	Nitrone sel. (%)	H_2O_2 eff. [b] (%)
TS-1	*t*-butanol	44	85	10	92
TS-1 [c]	*t*-butanol	51	96	–	87
none	*t*-butanol	16	15	35	27
none [c]	*t*-butanol	12	17	–	7
TS-1 [d]	*t*-butanol	70	28	72	60
TS-1	acetone	46	83	1	78
TS-2	acetone	46	90	2	89
TS-1 [d]	acetone	80	34	51	55
SiO_2–TiO_2 [e]	acetone	25	12	0	6
none	acetone	16	4	0	1
TS-1	methanol	43	87	13	97
none	methanol	21	84	9	43

[a] Catalyst weight (g) = 0.75, diethylamine (mmol) = 48, diethylamine : hydrogen peroxide (mol) = 2.0, solvent (ml) = 25, temperature (K) = 338, reaction time (h) = 1.

[b] H_2O_2 efficiency = (mol of hydroxylamine and nitrone formed/mol of hydrogen peroxide fed) × 100 (it is considered that 2 mol of hydrogen peroxide is utilized for nitrone).

[c] Data obtained from ref. [5] (1.5 g TS-1, 98 mmol diethylamine, 56 mmol hydrogen peroxide, 50 ml tert-butanol, 353 K).

[d] Diethylamine : hydrogen peroxide (mol) = 0.5.

[e] Shell catalyst (9% TiO_2) (ref. [14]).

of solvent and the concentration of hydrogen peroxide. The results reported in the patent literature are also provided. For the comparison, the results obtained in a blank run are also shown. H_2O_2 conversion was always 100%. When diethylamine to H_2O_2 molar ratio is 2, N,N′-diethyl hydroxylamine is formed very selectively. Another major product is diethyl nitrone. The only byproducts are from the oxidation at carbon atoms. Higher selectivity for hydroxylamine is observed, when methanol is used as a solvent. TS-1 and TS-2 catalysts exhibited similar conversion levels and the hydroxylamine selectivity. Very low selectivities obtained in the absence of any catalyst and even in the presence of amorphous SiO_2–TiO_2 clearly indicate that the isolated tetrahedral Ti^{4+} ions present in TS-1 and TS-2 are favorable active sites for this reaction.

When hydroxylamine is used as a substrate in a separate experiment (0.35 g TS-1, 2.14 g diethyl hydroxylamine, 2.33 g hydrogen peroxide, 25 ml tert-butanol at 338 K for 1 h), diethylnitrone is obtained in almost quantitative yields. This clearly indicates that nitrone is formed via hydroxylamine. Oxidation of diethylamine to nitrone is a faster reaction compared to that of diethylamine to hydroxylamine. At higher concentration of hydrogen peroxide (amine/H_2O_2 (molar) = 0.5), hydroxylamine is further oxidized to nitrone (table 1). These results demonstrate the feasibility of a direct oxidation of diethylamine to diethylnitrone in a single step.

Though, the patent literature claims the oxidation of larger molecules like dioctylamine and pyrrolidine, in the present study, it is found that dibutylamine (5%) and dipropylamine (10%) exhibited very low activity and the same conversions could be obtained even in the absence of any catalyst.

We have studied the oxidation of diethyl hydroxylamine to diethylnitrone in a DRS cell to monitor the reaction spectroscopically. The treatment of TS-1 with hydrogen peroxide resulted in the formation of peroxo titanium complex, characterized by an absorption at

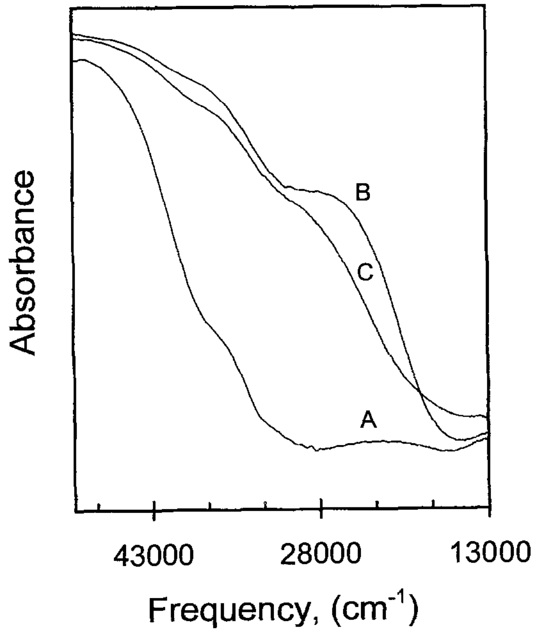
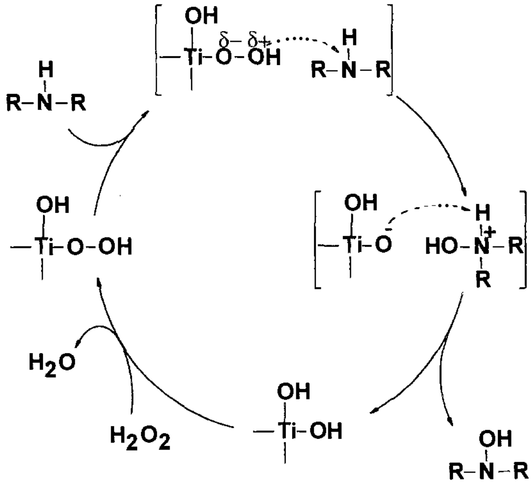


Fig. 1. Diffuse reflectance ultraviolet–visible spectra of (A): calcined TS-1, (B): TS-1 and hydrogen peroxide and (C): TS-1 treated with hydrogen peroxide and then diethylamine.

25 320 cm^{-1} (fig. 1) [4b]. When the H_2O_2–TS-1 sample was treated with diethyl hydroxylamine, the intensity of the band at 25 320 cm^{-1} decreased indicating that the peroxo titanium complex is involved in the oxidation of hydroxylamine and switched over to non peroxo titanium species. Fig. 2 reports the diffuse reflectance spectra of various samples in the near infrared region (5 000–7 500 cm^{-1}). The TS-1 sample treated with hydrogen peroxide exhibited a band at 7143 cm^{-1}, which can be assigned to the combination band of O–H absorption of hydrogen bonded water molecules. In addition to 2νO–H absorption at 7042 cm^{-1}, the TS-1 sample when treated with hydroxylamine showed two combination bands corresponding to C–H stretching of $-CH_3$ and $-CH_2-$ groups (5917 and 5780 cm^{-1}). When diethyl hydroxylamine is reacted with H_2O_2–TS-1, 2νO–H of hydroxylamine (7042 cm^{-1}) has disappeared immediately. This shows that hydroxylamine is converted to nitrone within a short reaction time.

A possible mechanism for the oxidation of secondary amine to the corresponding hydroxylamine is shown in scheme 1. In the mechanism of oxidation over titanium silicalites, a hydroperoxo titanium complex is known to be the active center [13]. The oxotitanium complex interacts with the secondary amine and inserts oxygen to give the corresponding hydroxylamine. Further oxidation of hydroxylamine with oxotitanium complex followed by dehydration yields nitrone.



Scheme 1.

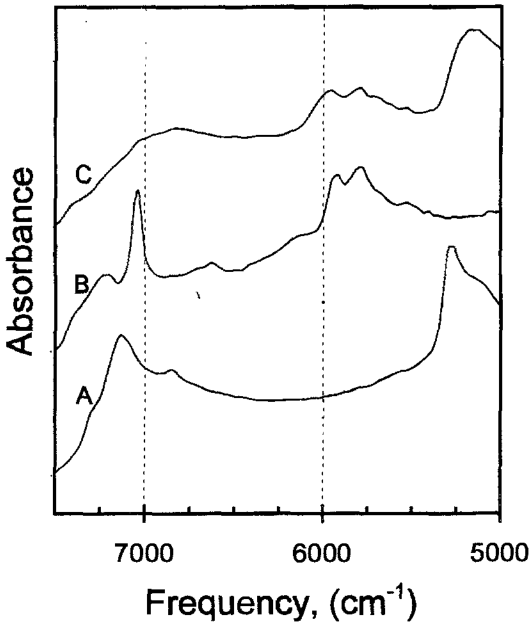


Fig. 2. Diffuse reflectance infrared spectra of various TS-1 samples in NIR region. (A): TS-1 with hydrogen peroxide, (B): TS-1 with diethylhydroxylamine, (C): TS-1 treated first with H_2O_2 and then diethylhydroxylamine.

4. Conclusions

Titanium silicalite molecular sieves, TS-1 and TS-2 are highly active and selective catalysts in the production of N,N′-diethyl hydroxylamine. They can also be used in the preparation of nitrones from hydroxylamines.

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