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Catalytic Selective Oxidation of Amines with Hydroperoxides over Molecular Sieves : Investigations into the Reaction of Alkylamines, Arylamines, Allylamines and Benzylamines with H_2O_2 and TBHP over TS-1 and CrS-2 as the new Catalyst†

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Abstract *: The liquid phase oxidation of various substituted amines with dil H_2O_2 and tert-butyl hydroperoxide (TBHP) has been investigated over titanium and chromium silicates respectively. While TS-1/H_2O_2 combination exhibits a remarkable activity and selectivity in the oxidation of arylamines to produce the symmetrical azoxybenzenes, CrS-2 catalyzes the selective oxidation of various substituted amines to the corresponding nitro compounds by oxidation with 70% TBHP. The nature of the reactive intermediates during the oxidation of anilines to nitrobenzenes has been established using cyclic voltammetry experiments. Further, amines possessing α C-H bonds are selectively oxidized to either oximes or the carbonyl compounds on reaction with H_2O_2 catalyzed by TS-1.*

1. INTRODUCTION

The oxidation of amines is an important reaction for fundamental and industrial applications, particularly for the synthesis of its oxygenated derivatives such as hydroxylamine, nitroso, nitro, oxime, azo and azoxy compounds. Among these, the preparations of nitro, oxime and azoxy compounds have assumed special importance as synthetically useful intermediates. Consequently, a variety of oxidation methods have been reported.[1] For example, arylamines can be oxidized not only with stoichiometric oxidants such as peracetic acid,[2] MnO_2[3], $Pb(OAc)_4$[4] and $Hg(OAc)_2$[5] but also with hydroperoxides by catalytic processes using t-BuOOH-M (M = Ti, Mo, W)[6], Ru-H_2O_2[7] etc. Obviously, the reaction selectivity to produce specific oxygenated product is of crucial importance. However, it is generally complicated by the several other competing reaction pathways resulting in the range of products of various oxidation states and the product composition depends as much on the reagent as on the structure of the amine itself. For instance, the oxidation of aniline with most of the known reagents generally results in a mixture of products comprising azobenzene, azoxybenzene, nitrosobenzene and nitrobenzene. At the same time, most of the existing methods are either non-catalytic or show poor selectivity in terms of product distribution.[8] Therefore, it assumes great importance to have effective control over selectivity in such reactions.

2. ZEOLITE CATALYSTS

During recent years, much effort has been devoted to the synthesis of metallosilicates with microporous structures. One approach to creating solid catalysts with novel activities is to incorporate redox metals, by isomorphous substitution, into the lattice framework of zeolites and related molecular sieves. The resulting redox molecular sieves may be regarded as 'mineral enzymes.'[9] Of late, redox zeolites like titanium and vanadium silicates

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with MFI and MEL topologies (TS-1, TS-2, VS-1 and VS-2) have been shown to possess unique catalytic properties in oxidation reactions with H_2O_2.[10] More recently, the incorporation of chromium into the silicalite-1 (CrS-1) and aluminophosphate (Cr AlPO-5) systems have been achieved.[11] Also we have reported quite recently the synthesis and characterization of chromium silicalite-2 (CrS-2) and its unique catalytic properties in the chemoselective epoxidation of alkenes with 70% TBHP as the oxidant.[12] It may be noted that the use of heterogeneous catalysts in the liquid phase offers several advantages compared with their homogeneous counterparts e.g. ease of recovery and recycling and enhanced stability.

In this paper, we wish to describe in detail the results on the chemistry of the oxidation of amines wherein the unique role of TS-1 and CrS-2 molecular sieves in controlling the reaction selectivity in combination with aq. H_2O_2 and TBHP as the oxidants has been demonstrated. Thus, arylamines are selectively oxidized to azoxybenzenes over TS-1 as the catalyst with H_2O_2. Whereas the same reaction displayed a dramatic change in reaction selectivity when switched over to CrS-2 - TBHP combination affording the products of higher oxidation state viz nitro compounds. Interestingly, the class of allyl and benzylamines showed an unprecedented selectivity in the formation of oximes with TS-1 - H_2O_2 combination.

3. RESULTS AND DISCUSSION

A. Oxidation of arylamines to azoxybenzenes : TS-1/H_2O_2[13]

Initially, a systematic investigation on the oxidation of aniline with different types of zeolites using H_2O_2 as the oxidant was undertaken (Table 1). The results clearly showed that H_2O_2 - TS-1 combination has exhibited higher activity and selectivity as compared to other molecular sieves, thus offering a new convenient reagent in directing the selective oxidation to azoxybenzenes in preparative yield. Unlike titanium molecular sieves, aluminosilicates are characterized by the presence of Lewis and Bronsted acid sites which are primarily responsible for the catalytic activity. Presumably, the low yields of product formation with these aluminosilicates could be attributed to the poisoning and deactivation of the catalyst upon long exposure to the nitrogen containing substrates.

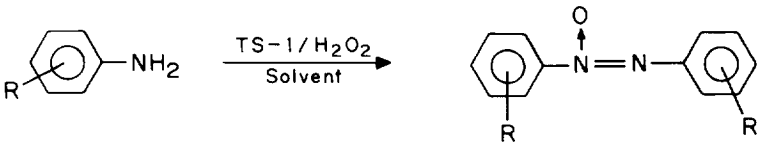
In order to study the scope and limitation of this reaction, various substituted aromatic amines were subjected to oxidation under the influence of TS-1 and the reaction was found to be quite a general one (Table 2, Scheme 1).

Table 1 : Zeolite catalyzed oxidation of aniline to azoxybenzene

Entry No.	Zeolite	Azoxybenzene Yield[a] (%)	Unreacted aniline[b] (%)
1.	No catalyst	25.5	43.4
2.	TS-1	87.8	9.2
3.	TS-2	64.2	29.2
4.	NaY	34.2	33.3
5.	HY	6.7	77.1

a : Determined by vapor phase chromatography

b : Unreacted aniline + unidentified products



1 (a-l) 2 (a-l)

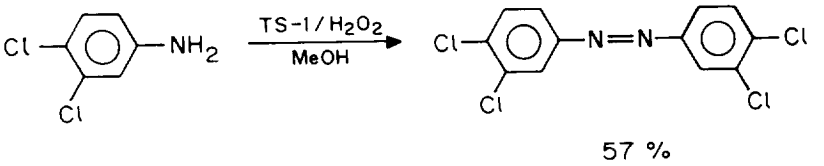
Scheme 1

Surprisingly, when arylamines having electron-withdrawing groups were subjected to oxidation with TS-1 - H_2O_2 system in acetone as solvent, no reaction took place. However, if methanol is used instead of acetone, these arylamines underwent oxidation rapidly to furnish symmetrical azoxybenzenes in moderate to good yields [entries i-k, Table 2]. Even naphthylamine was easily oxidized to the corresponding azoxy compound in 39% yield. In addition, 3,4-dichloroaniline underwent oxidation under the same reaction condition to yield only azobenzene in 57% yield (Scheme 2) with no trace of the corresponding azoxy obtained.

Table 2 : Oxidation of various arylamines with 30% H_2O_2 catalyzed by TS-1

Entry No.	Arylamine, 1 (a-l)	t/h	Solvent	Azoxybenzene 2 (a-l) Yield[a] (%)
a	Aniline	6	acetone	75
b	3-Methylaniline	5	acetone	41
c	3-Chloroaniline	6	acetone	44
d	4-Chloroaniline	5	acetone	55
e	2-Fluoroaniline	6	acetone	37
f	3-Methoxyaniline	5	acetone	54
g	4-Methoxyaniline	5	acetone	10
h	3-Nitroaniline	4	methanol	45
i	4-Nitroaniline	5	methanol	65
j	4-Aminobenzoic acid	5	methanol	72
k	1-Naphthylamine	5	methanol	39
l	Cyclohexylamine	6	acetone/methanol	No reaction

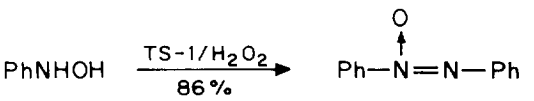
a : Isolated yield, the remainder is essentially unreacted aniline and other minor unidentified products.



Scheme 2

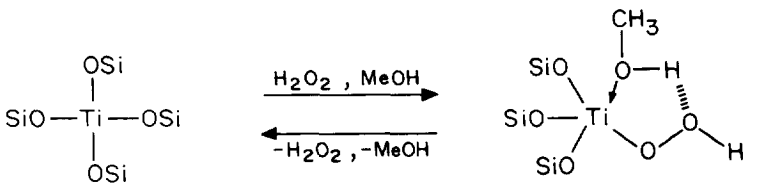
It may be noted that azoxybenzenes are used in organic synthesis and as dye intermediates. They are also used as initiator for polymerization and some derivatives of azoxybenzenes are used as liquid crystals in electronic display.[14]

Mechanism : In order to obtain more information on the reaction path of oxidation of amine, the likely intermediates such as phenylhydroxylamine, and azobenzene, presumably involved in the oxidation process, were subjected to oxidation with TS-1/H_2O_2 separately. The results shown in Scheme 3, indicate that phenylhydroxylamine is indeed the probable intermediate. It is, however, to be noted that azobenzene which was expected to be easily oxidized to azoxy, was resistant to further oxidation and was recovered unchanged, thus eliminating the possibility of involving azobenzene as the intermediate during azoxy formation.



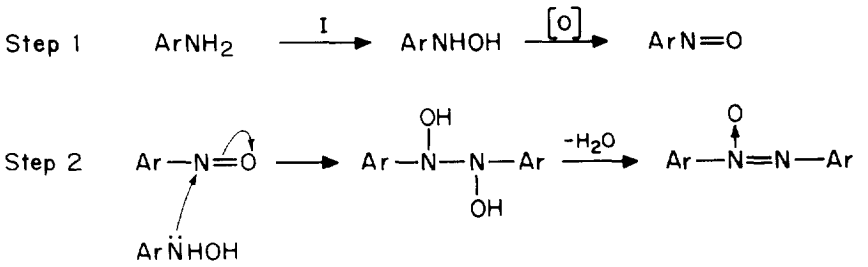
Scheme 3

Moreover, the fact that methanol has proved to be an excellent solvent for TS-1 catalyzed oxidations of arylamines with electron-withdrawing groups indicates that there may be some kind of coordination of methanol to the titanium metal providing stability to the Ti peroxo species (I).[15] Based on the above results, the following mechanism may be suggested (Scheme 4).



I

Peroxo species

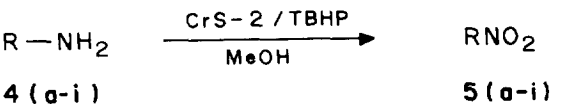


Scheme 4

B. **Oxidation of alkyl and arylamines to nitroalkanes and nitrobenzenes : CrS-2/TBHP**[16]

The direct oxidation of primary amines into the corresponding nitro derivatives is one of the most useful reactions for industrial applications and occupies a prominent position in synthetic organic chemistry. Although several reagent systems are known to effect such conversions, there are very few that are of practical value. Previously, such oxidations under stoichiometric conditions, have been performed mainly with peracetic acid, sodium perborate and dimethyl dioxirane[17] (for electron - donating substituent) or with peroxy trifluoroacetic acid and peroxydisulphuric acid[18] (for electron-deficient anilines). However, the difficulty in handling the hazardous nature of the anhydrous peracids and HOF[19] coupled with the prototropic rearrangement of nitroalkanes into oximes make the existing methods less than attractive.

As a part of our comprehensive ongoing programme on zeolite mediated organic reactions and as a logical extension of our work on the use of CrS-2/TBHP system, we subjected a variety of primary amines to oxidation with CrS-2/TBHP system to obtain the corresponding nitro compounds in high yields (Scheme 5).



R = alkyl , aryl

Scheme 5

Table 3 : Direct conversion of primary amines into nitro compounds with 70% TBHP over CrS-2

Entry No.	Amine 4 (a-i)	t/h	Product 5 (a-i)	Yield[a] (%)
a	Aniline	4	Nitrobenzene	92
b	4-Aminobenzoic acid	5	4-Nitrobenzoic acid	60
c	4-Nitroaniline	6	1,4-Dinitrobenzene	65
d	2-Cyanoaniline	7	2-Cyanonitrobenzene	52
e	Methylanthranilate	5	Methyl 2-nitrobenzoate	91
f	4-Methoxyaniline	3	4-Methoxynitrobenzene	80
g	Cyclohexylamine	5	Nitrocyclohexane	85
h	1-Aminobutane	5	1-Nitrobutane	80
i	Benzylamine	4	Benzaldoxime	76

a : Isolated after chromatographic purification

The results of CrS-2 catalyzed oxidations of primary amines with 70% TBHP at 65°C in MeOH are shown in Table 3. Remarkably, even arylamines with electron-withdrawing substituents such as COOH, NO_2, CN etc. (entries b-d) are efficiently oxidized to the corresponding nitroarenes, which otherwise may be difficult to obtain by the conventional nitration methods. In addition, aliphatic primary amines possessing α C-H bonds underwent oxidation selectively to afford the corresponding nitro derivatives without undergoing any kind of prototropic rearrangement to oximes. However, it may be noted that benzylamine, under the reaction conditions gave only the benzaldoxime in 76% yield.

Mechanism : When the oxidation of aniline with TBHP was carried out with TS-2 and VS-2 of similar topology, it is found that CrS-2 exhibits significantly better activity and selectivity (92%) than VS-2 (10%) while TS-2 totally failed to catalyze the reaction. In separate experiments, we have also shown that both phenylhydroxylamine and nitrosobenzene are readily oxidized to nitrobenzene by CrS-2/TBHP system indicating that the reaction might possibly proceed through the intermediates such as hydroxylamine and nitrosoalkane. Indeed, this is confirmed from cyclic voltammetry (CV) experiment (see experimental for details). The CV of aniline 10^{-2} mol) in Me CN (20 ml) containing tetrabutylammonium tetrafluoroborate (0.1 mol) and TBHP (10^{-2} mol) is shown in Fig.1.
It clearly indicates that there observed 3 peaks, two of them are irreversible peaks at + 980 mV and + 1300 mV and the other quasireversible peak (ΔE_p = 280 mV) observed with anodic peak at + 440 mV and cathodic peak at + 160 mV. This behavior indicates that there occurs a three-step oxidation of aniline to nitrobenzene involving phenylhydroxylamine and nitrosobenzene as intermediates.[20] Moreover, the g value of 1.97, in the ESR spectrum[12] of the calcined CrS-2 recorded at 293 K, is in the range reported for a variety of other stable and transient oxochromium (V) complexes.[21] Mechanistically, the oxochromium (V) species present in the zeolite framework appears to be responsible for its catalytic activity.

The selectivity differences between titanium silicalite and chromium silicalite towards the oxidation of amines can be explained by analogy with the catalytic property of Ti^{4+} and Cr^{5+} complexes in solutions. The redox potentials[22] of the Ti^{4+}/Ti^{3+} and Cr^{5+}/Cr^{4+} couples are 0.06 V and 0.50 V respectively. In general, the reducibility

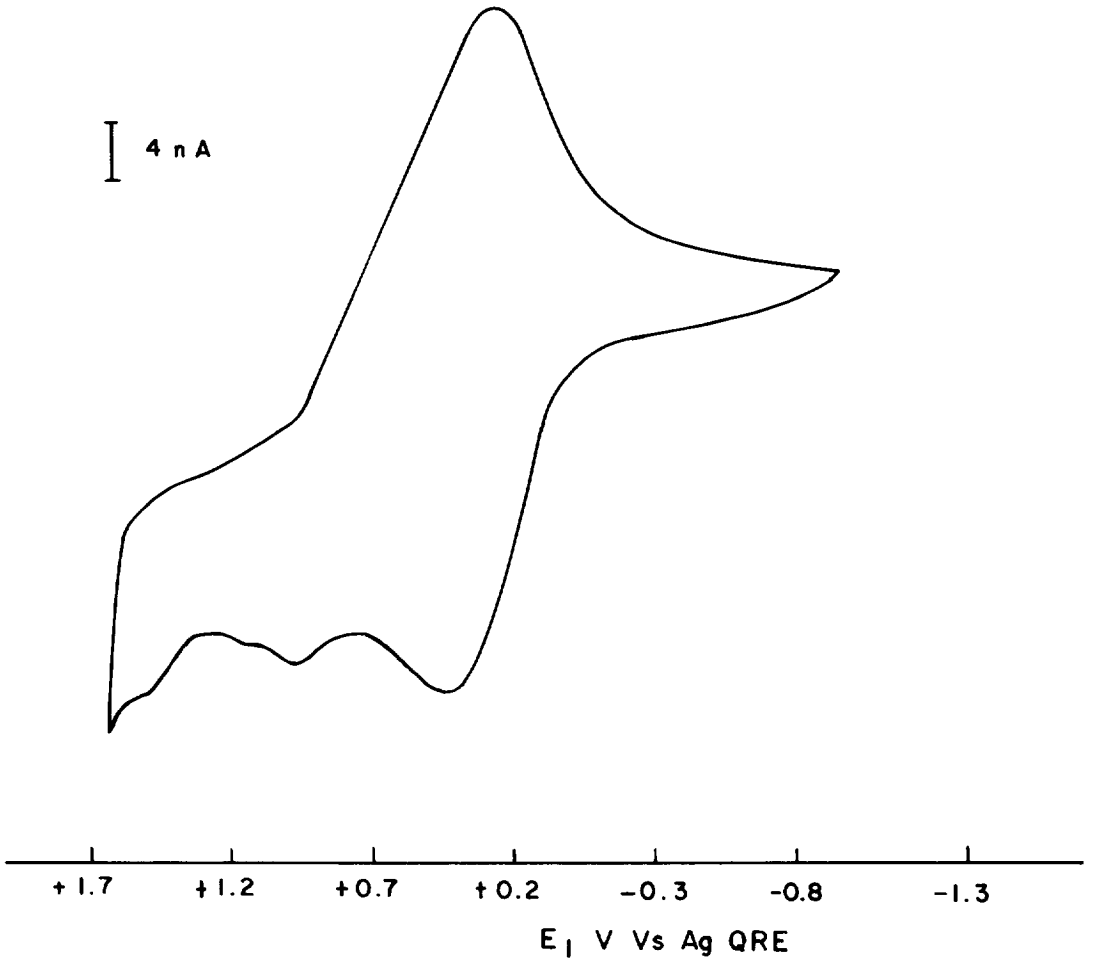


Fig.1 :Cyclic voltammogram of aniline in the presence of TBHP and tetrabutylammonium tetrafluoroborate using CrS-2 zeolite-modified Pt ultramicro electrode. Scan rate : 100 mV/sec.

of a metal ion is governed by its redox potential of the $M^{n+}/M^{(n-1)+}$ couple under the reaction conditions : the larger the redox potential, the larger its reducibility. The more easily reducible ions are more potent in decomposing ROOH.

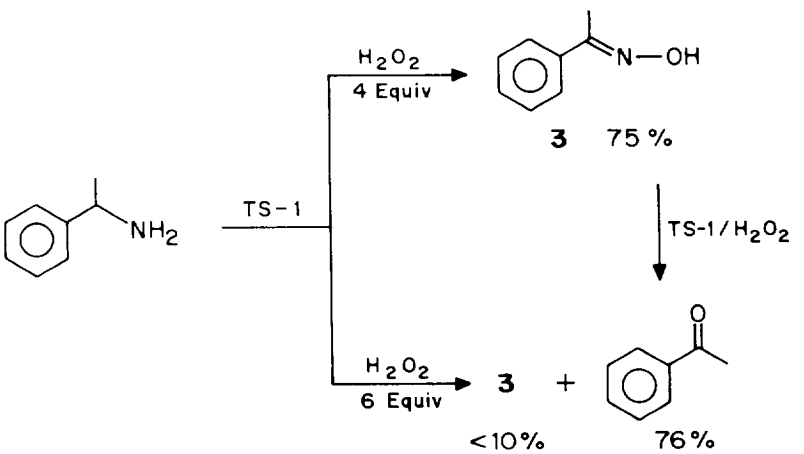
C. Oxidation of allylic and benzylic amines to oximes : TS-1/H_2O_2[23]

The oxidation of amines possessing α C-H bond activated by allylic or benzylic positions occupies a unique position in that there has always been a problem of exclusive production of one of the oxygenated products. For example, when such amines are oxidized, one would obtain a variety of higher oxygenated products such as hydroxylamine, nitroso compound or oxime (Equation I).

$$PhCH_2NH_2 \dashrightarrow PhCH_2NHOH \dashrightarrow PhCH_2N=O \dashrightarrow PhCH=NOH \ldots\ldots \quad I$$

Although such amines are readily oxidized by a range of reagents such as sodium salt of tungstic, molybdic or vanadic acids,[24] $NaBO_3$,[25] $R_2C(\mu\text{-}O_2)$,[26] PCWP-H_2O_2,[6] VS-1 - H_2O_2.[8] etc, there is a lack of general methodology for specific oxidative transformation of such amines to oximes. Further, the existing methods suffer from the following disadvantages : (1) oximes are obtained in low yields (2) oximes are produced along with other products so that separation becomes a problem and (3) most of the existing methods to produce oximes pertain to homogeneous, non-catalytic conditions.

In continuation of our work on the TS-1 catalyzed oxidation of amines, we subjected a variety of allylic and benzylic amines to oxidation with TS-1/H_2O_2. The results are summarized in Table 4. An interesting aspect to be noted in the present case is that the product selectivity is determined by the amount of H_2O_2 added (Scheme 6).



Scheme 6

With 4 moles of H_2O_2, it is possible to convert α-methylbenzylamine into the corresponding oxime in 75% yield. However, if 6 moles of H_2O_2 are used, the oxime undergoes oxidative cleavage to produce acetophenone in 76% yield in conformity with our earlier findings.[27] This turns out to be an important synthetic functional group transformation of converting an amine into a carbonyl function in a single step. It is remarkable that even cinnamylamine has been oxidized chemoselectively to cinnamaldehyde oxime in 50% yield. However, aliphatic amines possessing α C-H bond such as cyclohexylamine failed to undergo oxidation, although a very low yield of 3% (GC) has been reported by others[28] (Table 4). Mechanistically, the Ti peroxo species (I) oxidizes the N-H bond to produce R_1R_2 CHNHOH followed by its oxidation to R_1R_2 CHN=0 which then tautomerizes to oximes.

Table 4 : Oxidation of benzylic and allylic amines with 30% H_2O_2 catalyzed by TS-1

Entry No.	Substrate	H_2O_2 equiv.	Product	Yield[a] (%)
1	Benzylamine	4	Benzaldoxime	80
2	4-Methoxybenzylamine	4	4-Methoxybenzaldoxime	74
3	α-Methylbenzylamine	4	Acetophenone oxime	75
		6	Acetophenone oxime (<10%) + Acetophenone	76
4	3 (Aminomethyl) Pyridine	4	Pyridine-3-carboxaldoxime	75
5	1-Tetralylamine	4	1-Tetralone oxime	65
6	Cinnamylamine	4	Cinnamaldehyde oxime	50

a : Isolated yield after chromatographic purification.

4. CONCLUSION

In summary, we have shown that the oxidation of anilines with 30% H_2O_2 catalyzed by TS-1 in acetone or MeOH as solvent provides a simple, general procedure for the preparation of various substituted symmetrical azoxybenzenes. Whereas the CrS-2/TBHP combination has been shown to be an excellent catalytic system in selectively oxidising anilines into nitro compounds. The nature of the reactive intermediates during the oxidation of anilines to nitrobenzenes has been confirmed by cyclic voltammogram. Further, we have shown that TS-1 is an efficient catalyst in converting primary amines possessing α C-H bond directly to either oxime or the carbonyl compound selectively depending upon the amount of H_2O_2 used, thus constituting an excellent catalytic method of converting an amino function into a carbonyl group directly in synthetically useful reactions.

Acknowledgement

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EXPERIMENTAL

All mps reported are uncorrected. IR spectra were recorded as neat or nujol mulls (in case of solid samples) on Perkin-Elmer Infrared model 137-E. ^1H NMR spectra were taken on a Varian FT 80A, Bruker FT 90, 200 MHz instruments. ^{13}C NMR were obtained on a Bruker 200 MHz instrument. The chemical shifts were reported with TMS as the internal standard. The mass spectra (MS) were recorded on an automated Finnigan MAT 1020 C mass spectrometer using ionization energy of 70 eV.

Synthesis of Chromium Silicalite-2 (CrS-2) : The zeolite CrS-2 was hydrothermally synthesized[16] using gels of the following compositions : SiO_2 : x Cr_2O_3 : 0.4 TBAOH : 30 H_2O. Crystallization was performed at 443 K for 90 h. The crystalline material was subsequently calcined at 773 K for 5 h. The chemical analysis of the calcined CrS-2 sample gave Si : Cr = 140:1. This sample was further characterized by XRD, IR, ESR and SEM techniques.

Preparation of TS-1, TS-2, NaY, HY and VS-2 : For TS-1 and TS-2, see Thangaraj, A, Kumar R, Mirajkar, S.P. and Ratnasamy, P. *J.Catal*, 1991, **130**, 1. Reddy, J.S., Kumar, R, and Ratnasamy, P. *Appl.Catal*, 1990, **58**, L1; Reddy, J.S. and Kumar, R. *J.Catal*, 1991, **130**, 440; Reddy, J.S., Sivasanker, S. and Ratnasamy, P. *J.Mol.Catal*, 1991, **69**, 383; The zeolites Na-Y and H-Y were purchased from Union Carbide, USA. For VS-2, see Hari Prasad Rao, P.R., Ramaswamy, A.V. and Ratnasamy, P., *J.Catal.* 1992, **137**, 225.

General procedure for the oxidation of anilines to azoxybenzenes : In a typical reaction, 30% aqueous H_2O_2 (0.075 mol) was added dropwise to a mixture of aniline (0.05 mol) and the catalyst, TS-1 (1.0 g) in either acetone or MeOH (25 ml) and the reaction mixture was refluxed for 4-6 h. After the reaction was complete, the catalyst was filtered off and the crude reaction products were purified by flash chromatography, readily identified by their physical and spectral properties and by comparison with the reported values.

Azoxybenzene (2a) : m.p. 38°C (lit. 38.5 - 39°C); IR (Nujol) : 1485, 1450, 1325, 1170, 1080, 1035, 940, 915, 770 and 695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) : δ 7.31 - 7.62 (5H, m), 8.12 - 8.44 (5 H, m); ^{13}C NMR (90 MHz, $CDCl_3$) : δ 125, 125.2, 128.0, 128.2, 128.4, 128.9, 130.8, 143.3 and 147.6; MS : m/z (rel. intensity) 198 (M^+, 68), 182 (6), 169 (45), 152 (6), 141 (30), 115 (13), 105 (45), 91 (60), 77 (100), 65 (12).

3,3' - Dimethylazoxybenzene (2 b) : m.p. 40°C (lit. 39°C); IR (Nujol) : 1535, 1500, 1440, 1360, 1100, 810, 740 and 695 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 2.44 (6 H, s, 2 x CH_3). 7.18 - 7.5 (4 H, m), 7.93 - 8.18 (4 H, m); MS : m/z (rel. intensity) 137 (36), 107 (10), 91 (100), 77 (22) and 65 (94).

3,3' - Dichloroazoxybenzene (2 c) : m.p. 95-96°C (lit. 97°C); IR (Nujol) : 1520, 1465, 1210, 1080, 1010, 890, 800 and 685 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 7.25 - 7.50 (4 H, m), 7.75 - 8.32 (4 H, m);MS : m/z (rel. intensity) 268 (M+2, 6), 266 (M^+, 12), 250 (4), 231 (2), 203 (4), 168 (5), 139 (12), 125 (18), 113 (32), 111 (100), 99 (20), 90 (11), 85 (11), 75 (58), 63 (26).

4,4' - Dichloroazoxybenzene (2 d) : m.p. 155°C (Lit. 158°C); IR (Nujol) : 1590, 1470, 1410, 1320, 1310, 1290, 1165, 1095, 1015, 920, 835 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 7.5 (4 H, dd, J = 8 and 4 Hz), 8.25 (4H, dd, J = 8 and 4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) : δ 123.9, 127.2, 129.1, 129.2, 135.4, 138.3, 142.5; MS : m/z (rel. intensity) 268 (M+2, 16), 266, (M^+, 26), 250 (2), 203 (5), 168 (4), 139 (12), 125 (36), 113 (31), 111 (100), 99 (16), 90 (26), 75 (48), 63 (22).

2,2' - Difluoroazoxybenzene (2 e) : m.p. 48°C (Lit 48.5°C); IR (Nujol) : 1615, 1500, 1470, 1340, 1280, 1250, 1120, 1090, 1040, 920, 830 and 695 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 7 - 7.62 (6H, m), 7.75 - 8.12 (1 H, m), 8.2 - 8.4 (1H, m); ^{13}C NMR (200 MHz, $CDCl_3$) : δ 115.7, 116.2, 117.3, 117.7, 123.8, 124.0, 124.2, 125.3, 130.3, 130.4, 132.1, 132.3; MS : m/z (rel intensity) 234 (M^+, 100), 214 (48), 185 (8), 159 (5), 139 (17), 123 (15), 109 (38), 95 (25), 75 (6).

3,3' - Dimethoxyazoxybenzene (2 f) : m.p. 50°C (Lit. 51°C); IR (Neat) : 1620, 1480, 1330, 1270, 1155, 1050, 870, 790 and 695 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 3.75 (6 H, s, OMe), 6.75 (8 H, m); MS : m/z (rel. intensity) 258 (M^+, 13), 242 (15), 230 (8), 215 (7), 188 (25), 135 (12), 107 (100), 92 (57), 77 (73), 71 (26), 64 (40), 57 (36).

4,4' - Dimethoxyazoxybenzene (2 g) : m.p. 115-117°C (Lit. 118°C); IR (Nujol) : 1600, 1570, 1460, 1390, 1270, 1030, 850 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) : δ 3.84 (6H, s, OMe), 6.9 (4 H, dd, J = 10 and 2 Hz), 8.15 (4H, dd, J = 11 and 4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) : δ 55.7, 113.8, 113.9, 114.4, 124.0, 124.5, 128.0, 147.4, 160.4, 161.8; MS : m/z (rel. intensity) 258 (M^+, 8), 242 (31), 226 (8), 213 (15), 199 (29), 198 (25), 187 (18), 184 (36), 167 (9), 149 (15), 135 (45), 121 (23), 107 (100), 92 (18), 83 (8).

3,3' - Dinitroazoxybenzene (2 h) : m.p. 141°C (Lit. 143°C); IR (Nujol) : 1530, 1460, 1380, 1350, 1080, 920 and 820 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$ + DMSO-d_6) : δ, 7.8 (2H, m), 8.3 (3H, m), 8.55 (1H, d, J = 7.5 Hz), 8.65 (1H, b.s), 9.05 (1H, b.s); MS : m/z (rel. intensity) 288 (M^+, 10), 272 (10), 166 (4), 150 (49), 137 (32), 122 (100), 107 (5), 95 (44), 81 (15), 76 (60), 63 (32) and 57 (20).

4,4' - Dinitroazoxybenzene (2 i) : m.p. 191°C (Lit. 192°C); IR (Nujol) : 1520, 1460, 1380, 1340, 1100, 860, 720 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) : δ 8.3 (4H, s), 8.5 (4H, d, J = 8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) : δ 123.4, 123.7, 124.0, 125.7; MS : m/z (rel. intensity) 288 (M^+, 8), 271 (5), 166 (4), 150 (39), 139 (5), 122 (100), 110 (15), 92 (60), 80 (41), 76 (68), 75 (72) and 63 (59).

4,4'- Dicarboxylic acid azoxybenzene (2 j) : m.p. > 280°C decomposes (Lit. 240°C decomp. and 350-55°C decomp.); IR (Nujol) : 3400 - 3300, 1700, 1600, 1460, 1380, 1280, 1120, 940, 860, 770 cm^{-1}; ^1H NMR (200 MHz, DMSO - d_6) : δ 8.0 (2H, s), 8.15 (4H, m), 8.6 (2H, d, J = 8.5 Hz); MS : m/z (rel. intensity) 286 (M^+, 9), 258 (9), 213 (3), 149 (21), 137 (5), 121 (70), 109 (8), 93 (10), 81 (12), 76 (15), 65 (100).

1,1' - Azoxynaphthalene (2 k) : m.p. 123°C (Lit 127°C); IR (Nujol) : 1460, 1360, 1020, 910, 800, 760, 740 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) : δ 7.6 (6H, m), 7.95 (5H, m), 8.35 (1H, m), 8.55 (1H, m), 9.2 (1H, d, J = 6 Hz).

2,2',3,3' - Tetrachloroazobenzene : m.p. 174°C; ^1H NMR (200 MHz, $CDCl_3$) : δ 7.4 (2H, dd, J = 8 Hz and 2 Hz), 7.65 (2H, d, J = 2 Hz), 7.8 (2H, d, J = 8 Hz); MS : m/z (rel. intensity) 324 (M+4, 2), 323 (M+3, 1), 322 (M+2, 8), 321 (M+1, 4), 320 (M^+, 18), 175 (38), 173 (64), 147 (60), 145 (100), 109 (47), 74 (22).

General procedure for the oxidation of amines to nitro compounds : In a typical reaction procedure, a mixture of aniline (0.93 g, 10 mmol), CrS-2 (93 mg, 10% wt/wt) and 70% TBHP (4.5 ml, 33 mmol) in MeOH (25 ml) was heated under reflux for 4h. After the reaction was complete (TLC), the catalyst was filtered off and the product purified by flash chromatography to afford nitrobenzene (1.13 g, 92%).

Nitrobenzene : IR (Neat) : 1610, 1490, 1320, 1100, 1060, 860 and 790 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) : δ 7.5 (2H, m), 7.75 (1H, b.t), 8.3 (2H, d, J = 8 Hz).

4-Nitrobenzoic acid m.p. 239°C (Lit. 239-240°C); IR (Nujol) : 3400-2400, 1690, 1610, 1530, 1450, 1300, 1180, 1115, 950, 860, 730 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 8.3 (4H, s), 8.6 (1H, s, OH exchangeable with D_2O).

1,4 - Dinitrobenzene : m.p. 173°C (Lit. 172-174°C); IR (Nujol) : 1610, 1550, 1350, 1215, 1100, 1030, 990, 860, 840 and 760 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 8.45 (4H, s).

2-Cyanonitrobenzene : m.p. 104-106°C (Lit. 104-106°C); IR (Nujol) : 2220, 1610, 1580, 1520, 1450, 1370, 1320, 1260, 1200, 1150, 1070, 970, 880, 760 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 7.8 - 8.1 (3H, m), 8.3 - 8.5 (1H, m).

Methyl 2-nitrobenzoate : Liquid, 100-110°C/0.1 mm; IR (Nujol) : 1735, 1600, 1520, 1450, 1370, 1300, 1250, 1200, 1120, 960, 870, 760, 700 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 3.9 (3H, s, OMe), 7.5 - 7.8 (4H, m, Ar-H).

4-Methoxynitrobenzene : m.p. 50°C (Lit. 50-52°C); IR (Nujol) : 1560, 1430, 1310, 1240, 1060, 980, 830 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 3.9 (3H, s, OMe), 6.9 (2H, d, J = 8 Hz), 8.1 (2H, d, J = 8 Hz).

Nitrocyclohexane : Liquid; 110-120°C/0.1 mm; IR (Neat) : 1550, 1460, 1380, 1250, 1160, 900, 740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) : δ 1.1 - 1.2 (4H, m, 2 x CH_2), 1.6 - 1.9 (4H, m, 2 x CH_2), 2.0 - 2.3 (2H, m, CH_2), 4.1 - 4.5 (1H, m, CH).

1-Nitrobutane : Liquid; 70-80°C/10-12 mm; IR (Neat) : 1500, 1410, 1360, 1270, 1110, 790 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) : δ 0.85 (3H, t, J = 6 Hz, CH_3), 1.4-1.5 (2H, m, CH_2), 2.2 (2H, m, CH_2), 2.8 (2H, t, J = 6 Hz, CH_2).

General procedure for the oxidation of benzylic and allylic amines to oximes : In a typical reaction, a mixture of benzylamine (0.535 g, 5 mmol), TS-1 (53 mg, 10% wt/wt) and 30% H_2O_2 (2.2 ml, 20 mmol) in MeOH (15 ml) was refluxed for 4h. After the reaction was complete (TLC), the catalyst was filtered off and the product purified by flash chromatography to afford benzaldoxime (0.484 g, 80%).

Benzaldoxime : Liquid; IR (Neat) : 3400-3100, 1650, 1500, 1450, 1310, 1220, 960, 910, 870, 730, 690 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 6.5 (1 H, br.s, OH), 7.0 - 7.3 (5H, m, ArH) and 8.0 - 8.19 (1H, s, = C - H).

4-Methoxybenzaldoxime : m.p. 65°C (Lit. 65°C); IR (Nujol) : 3300 - 3100, 1450, 1360, 1300, 1060, 1000, 920, 750 and 690 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) : δ 4.03 (3H, s, OMe), 7.06 (2H, d, J = 10 Hz), 7.7 (2H, d, J = 10 Hz), 8.2 (1H, s, = C - H), 9.1 (1H, b.s., OH exchangeable with D_2O).

Pyridine-3-carboxaldoxime : m.p. 146°C (Lit. 150°C); IR (Nujol) : 3300-3100, 1600, 1420, 1300, 1220, 1030, 980, 760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$ + DMSO-d_6) : δ 7.15 (1H, m), 7.8 (1H, d, J = 4 Hz), 8.3 (1H, br.s), 8.6 (1H, br.s) and 10.9 (2H, br.s, OH, exchangeable with D_2O); ^{13}C NMR (200 MHz, $CDCl_3$) : δ124.3, 129.5, 133.6, 146.3, 148.3 and 150.3.

1-Tetralone oxime : m.p. 92°C (Lit. 89°C); IR (Nujol) : 3400-3200, 1610, 1450, 1360, 1270, 1050, 970, 900 and 750 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) : δ 1.8 - 2.0 (2H, m, CH_2), 2.6 - 2.9 (4H, m, 2 x CH_2), 5.5 (1H, br.s, OH), 7.0 - 7.2 (3H, m, Ar H) and 7.9 (1H, m, Ar H).

Cinnamaldehyde oxime : m.p. 138°C (Lit. 139°C), IR (Nujol) : 3250 - 3100, 1620, 1450, 1360, 1350, 1310, 1140, 980, 930, 750 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) : δ 6.75 (1H, d, J = 14 Hz, CH), 7.2 - 7.5 (6H, m), 8.1 (1H, s).

Cyclic Voltammetry Experiment

Cyclic voltammetry (CV) experiments were carried out in a three compartment cell with zeolite modified Pt ultramicro electrode as working electrode. It is prepared[29] as follows. The zeolite CrS-2 (100 mg), graphite (100 mg) and polystyrene as binder (10 mg) were made into a thorough paste and coated at the tip of a platinum ultramicro electrode of radius 10 μm. The CV experiments were carried out in 0.1 molar tetrabutylammonium tetrafluoroborate as supporting electrolyte in MeCN using Pt wire as counter electrode and Ag wire as quasi reference electrode. All the measurements were carried out in argon at 25°C using a PAR 173 potentiostat coupled with 173 universal function generator and model RE 0091 X-Y recorder.

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