

Selective Catalytic Oxidation of Arylamines to Azoxybenzenes with H₂O₂ over Zeolites†

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Catalytic version of the H₂O₂-TS-1 combination has been shown to display a good reaction selectivity in the liquid-phase oxidation of anilines to symmetrical azoxybenzenes.

The oxidation of arylamines has attracted considerable attention for quite some time and several methods of oxidation have been reported.¹ Most of these are non-catalytic and the product range corresponds to various oxidation states depending upon the nature of the reagent, viz. MnO₂,² RCOOOH,³ O₃,⁴ R₂C(μ-O₂), Bu^uOOH-Mo^{VI}, V^V,⁶ Bu^uOOH-Ti^{IV},⁷ H₂O₂-RuCl₃-PTC,⁸ etc. In view of the current interest in catalytic processes, it is appropriate to develop a true catalytic oxidation reaction of arylamines using inexpensive and non-polluting reagents. In this context, a recent report⁹ on this topic prompted us to communicate our results. The above mentioned report concerns the cetylpyridiniumheteropolyoxometalate (PCWP)-catalyzed oxidation of anilines by H₂O₂ (30%) wherein reaction parameters such as temperature and medium have been shown to direct the reaction selectivity mostly in favour of one or other of the oxidation products, viz. nitrosobenzene, azoxybenzene and nitrobenzene.

Catalytic oxygen transfer¹⁰ involving the reaction of an oxygen donor with an organic substrate in the presence of a catalyst holds considerable promise in commercial oxidation reactions. Zeolites are endowed with distinct structures and unique properties attributed to the presence of intracrystalline cavities. In recent years, the zeolites, TS-1 (MFI) and TS-2 (MEL) have figured prominently for their remarkable catalytic properties when used with dilute H₂O₂ (≈30%) as oxidant.^{10,11} As part of our comprehensive ongoing programme on zeolites at this laboratory, we wish to report a new catalytic method for selective oxidation of anilines to azoxybenzenes using titanium silicate molecular sieve (TS-1) and dilute H₂O₂ employing acetone as solvent.

It may be mentioned that there are some naturally occurring azoxybenzenes which possess potent biological properties.¹² Also, metal-catalyzed oxidation of amines is of interest because of its relevance to the enzymatic degradation of nitrogen-containing compounds in biological systems. Their utility in liquid crystals is also well known.¹³

The zeolite catalysts TS-1,¹⁴ TS-2,¹⁵ Na-Y,¹⁶ La (80) Al-ZSM-5¹⁷ and H-Y¹⁶ were synthesized following literature procedures. In a typical reaction, aqueous H₂O₂ (30%, 0.05 mol) was added dropwise to a mixture of aniline (0.05 mol) and the catalyst (1.0 g) in acetone (25 ml) and the reaction mixture was refluxed for 5–6 h. The crude reaction products were purified by flash chromatography and were readily identified by their physical and spectral properties and by comparison with the reported values.¹⁹ The results are summarized in Tables 1 and 2.

Notably, the titanium silicates exhibit better activity and selectivity as compared to other aluminosilicates studied here and lead to the formation of azoxybenzenes in preparative yields (Table 1). This result thus illustrates another example of the efficacy of this catalytic system which has been shown to be important for several commercial oxidation reactions in recent years.¹⁰ It may be mentioned here that 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 the case of 4-methoxyaniline, the yield was rather low

owing to the formation of many unidentified side products. Also, cyclohexylamine under the reaction conditions, failed to undergo oxidation.

The peroxy-species, >Ti(μ-O₂), generated *in situ* upon reaction of the silica-bound titanyl (>Ti=O) active site with H₂O₂ followed by elimination of water, is believed to provide the reactive O* species for oxidation.¹⁸ Work is in progress to gain further insight into the mechanistic aspects of this process.

In summary, the results described herein demonstrate the novelty of TS-1 catalyst which exercises unique selectivity in the oxidation of anilines to azoxybenzenes by dilute H₂O₂.

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Table 1 Zeolite catalyzed oxidation of aniline to azoxybenzene

Entry	Zeolite	Ph-NH ₂ $\xrightarrow[\text{acetone, reflux}]{\text{H}_2\text{O}_2/\text{Zeolite}}$ Ph-N=N-Ph	
		Azoxybenzene yield ^a (%)	Unreacted aniline ^b (%)
1	No catalyst	25.5	43.4
2	TS-1 ¹⁴	87.8	9.2
3	TS-2 ¹⁵	64.2	29.2 ²⁰
4	Na-Y ¹⁶	34.2	33.3
5	La(80)Al-ZSM-5 ¹⁷	17.3	49.6
6	H-Y ¹⁶	6.7	77.1

^a Determined by vapour-phase chromatography.

^b Unreacted aniline + unidentified products.

Table 2 Oxidation of anilines with H₂O₂ catalyzed by zeolite, TS-1

Entry	Substrates, 1 Ar	Ar-NH ₂ $\xrightarrow[\text{reflux}]{\text{H}_2\text{O}_2}$ Ar-N=N-Ar		
		t/h	Product ^a , 2; Yield ^b (%)	Mp ¹⁹ /°C (lit.) ^c
1	Phenyl	6	75	38 (39)
2	3-Methylphenyl	5	41	40 (39)
3	3-Methoxyphenyl ^c	5	54	50 (51)
4	4-Methoxyphenyl	5	10	117 (118)
5	3-Chlorophenyl	6	44	96 (97)
6	4-Chlorophenyl ^c	5	55	155 (158)
7	2-Fluorophenyl	6	37	48 (48.5)
8	Cyclohexylamine	6	No reaction	—

^a Characterised by IR, ¹H and ¹³C NMR and MS. ^b Isolated yield, the remainder is essentially unreacted aniline and other minor unidentified products. ^c The zeolite catalysts were recovered and reused three times with virtually no loss of activity.

Footnote

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References

- 1 T. L. Gilchrist, in *Comprehensive Organic Synthesis* ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 7, p. 735; D. H. Rosenblatt and E. P. Burrows, in *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*, ed. S. Patai, Wiley, Chichester, 1982, p. 1085.
- 2 O. D. Wheeler and D. Gonzales, *Tetrahedron*, 1964, **20**, 189.
- 3 R. R. Holmes and R. P. Bayer, *J. Am. Chem. Soc.*, 1964, **82**, 3454.
- 4 P. S. Bailey, *Ozonation in Organic Chemistry*, Academic Press, New York, 1982, vol. 2, p. 155.
- 5 R. W. Murray, S. N. Rajadhyaksha and L. Mohan, *J. Org. Chem.*, 1989, **54**, 5783.
- 6 G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, 1970, **25**, 4007.
- 7 K. Kosswig, *Justus Liebigs Ann. Chem.*, 1971, **749**, 206.
- 8 G. Barak and Y. Sasson, *J. Org. Chem.*, 1989, **54**, 3484.
- 9 S. Sakaue, T. Tsubakino, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 1993, **58**, 3633.
- 10 R. A. Sheldon, *Chemtech*, 1991, 566.
- 11 R. S. Reddy, J. S. Reddy, R. Kumar and P. Kumar *J. Chem. Soc., Chem. Commun.*, 1992, 84; M. Narayana Rao, P. Kumar, A. P. Singh and R. S. Reddy, *Synth. Commun.*, 1992, **22**, 1299; J. S. Reddy, U. R. Khire, P. Ratnasamy and R. B. Mitra, *J. Chem. Soc., Chem. Commun.*, 1992, 1234.
- 12 *Biological Oxidation of Nitrogen in Organic Molecules*, ed. J. W. Gorrod and L. A. Damani, Ellis Horwood, Chichester, 1985; S. Murata, M. Miura and N. Nomura, *J. Org. Chem.*, 1989, **54**, 4700.
- 13 J. P. Snyder, V. T. Bandurco, F. Darack and H. Olsen, *J. Am. Chem. Soc.*, 1974, **96**, 5158.
- 14 M. Taramasso, G. Perego and B. Notari, *US Pat.* 4 410 501, 1983; A. Thangaraj, R. Kumar, S. P. Mirajkar and P. Ratnasamy, *J. Catal.*, 1991, **130**, 1.
- 15 J. S. Reddy, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 1990, **58**; L1; J. S. Reddy and R. Kumar, *J. Catal.*, 1991, **130**, 440; J. S. Reddy, S. Sivasankar and P. Ratnasamy, *J. Mol. Catal.*, 1991, **69**, 383.
- 16 The zeolites Na-Y and H-Y were purchased from Union Carbide, USA.
- 17 Patent is filed under Indian Patent Act. *Indian Pat.* 164416, 1988.
- 18 B. Notari, in *Innovation in Zeolite Materials Science* ed. P. J. Grobet, W. J. Mortier, E. F. Vansant, G. Schultz-Ekloff, B. S. Delmon and J. Yates, Elsevier Science Publishers, Amsterdam, 1987.
- 19 *Dictionary of Organic Compounds* ed. J. Buckingham, 5th edn., Chapman and Hall, New York, 1982; for fluoro derivatives; see G. Olah, A. Pavlath and T. Kuhn, *Chem. Abstr.*, 1956, 11261 h.
- 20 Patent is filed under Indian Patent Act 1992, 527, 929 DEL/92.