A new catalytic method for the selective oxidation of aniline to nitrosobenzene over titanium silicate molecular sieves, TS-1, using H_2O_2 as oxidant

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The oxidation of aniline to nitrosobenzene with a selectivity > 73% has been achieved using titanium silicate molecular sieves, TS-1 as catalyst and aqueous H_2O_2 as oxidant at 273 K in a batch reaction.

Aromatic nitroso compounds are used in the vulcanization of rubber, stabilization of halogenated materials and as antioxidants in lubricating oil.[1] Several homogeneous catalytic methods have been reported in the literature on the oxidation of aromatic primary amines to their corresponding nitroso compounds. These include use of H_2SO_4–H_2O_2–CH_3CO_2H,[2] peroxotungstophosphate(PCWP)–H_2O_2,[3] $Mo(O)(O_2)_2(H_2O)$-(hmpa)–H_2O_2,[4] $Pb(OAc)_4$[5] and $FeCl_3$[6] as catalysts. Nitroso compounds are also produced by the direct reduction of nitro compounds with Mn_3O_4.[7] The discovery of titanium silicate molecular sieves with MFI (Mobile Five) structure, TS-1, has opened up a new area in the selective oxidation of organic compounds, such as the oxyfunctionalization of alkanes,[8] epoxidation of alkenes,[9] sulfoxidation of thioethers[10] and hydroxylation of phenol[11] using aqueous H_2O_2 as oxidant. Although more than 80% yield of aromatic nitroso compounds can be achieved by the existing homogeneous catalytic methods, the use of titanium silicate molecular sieves provides a better alternative to the problems of catalyst recovery, requirement of a stoichiometric amount of the homogeneous catalyst, separation of the products and the corrosive nature of the catalyst *etc*., caused by the homogeneous system.

Recently, it has been reported that TS-1 is an excellent catalyst for the selective oxidation of aniline to azoxybenzene using H_2O_2 as oxidant.[12,13] The oxidation of alkylamine to the corresponding oximes over TS-1 has also been communicated by Reddy and Jacobs.[14] Up until now, all the liquid phase oxidations of different organic compounds have been carried out over TS-1 either at room temperature or at reflux temperatures. For the first time, we herein present the potential of the TS-1 system, in the selective oxidation of aniline to nitrosobenzene at 273 K.

Vanadium incorporated silicalites (VS-1) and the silica polymorph of ZSM-5 (Si-1) have been used to highlight the unique catalytic behaviour of TS-1. TS-1, VS-1 and Si-1 samples were synthesized hydrothermally according to the published procedures.[15–17] The Si/Ti and Si/V ratios were 45 and 80, respectively. The samples were further characterized by XRD, IR, SEM, UV and adsorption techniques. The surface area, micropore volume and sorption capacities are indicative of the purity of these metallosilicates prepared. The catalytic reactions were carried out batchwise in a 50 ml round bottomed flask with continuous stirring (700 rpm) in the temperature range of 273–313 K. In a typical run, 100 mg of the catalyst was dispersed in a solution containing 10 mmol of aniline, 10 mmol of H_2O_2 (30% aqueous solution) and 20 ml of a solvent (acetonitrile). After completion of the reaction (about 5 h), the products were analysed in a capillary gas chromatograph (HP 5880), fitted with a 50 m long cross linked methyl silicone gum capillary column. The identity of the products were established by GC–MS (Shimadzu, QP 2000 A).

The results of the oxidation of aniline with different H_2O_2–aniline ratios, solvents and catalysts are summarised in Table 1. At 273 K and using acetonitrile as solvent, 7.3 mol% conversion of aniline with a high selectivity for nitrosobenzene (72.4%) is obtained. Among the solvents tested in this selective oxidation of aniline to nitrosobenzene, acetonitrile is found to be the best. The extent of conversion of aniline in different solvents is found to be in the order acetone > methanol > water > acetonitrile > *tert*-butyl alcohol. However, the selectivity towards nitrosobenzene in the final product is found to be in the order acetonitrile > methanol > *tert*-butyl alcohol > water > acetone. In the presence of acetone, formation of imine and their hydroxylated products results in poor selectivity to nitrosobenzene (7.2%).

In order to improve the conversion of aniline, the H_2O_2–aniline ratios were varied from 1 to 3. As expected, an increase in the conversion from 7.3 to 10.2 mol% is observed. However, the selectivity to nitrosobenzene decreased from 72.4 to 67.0%

Table 1 Oxidation of aniline with different H_2O_2–aniline ratios, solvents and catalysts.[a]

				Product distribution (%)[b]						
Catalyst	Solvent	H_2O_2–aniline (mol ratio)	Conv. (mol%)	NSOB	NB	OAP	PAP	AB	AXYB	Others[c]
TS-1	Acetonitrile	1	7.3	72.4	1.4	0.2	0.3	3.3	22.4	—
TS-1	Acetonitrile	2	8.9	68.5	3.4	1.1	0.6	2.3	23.5	0.6
TS-1	Acetonitrile	3	10.2	67.0	2.3	0.5	0.4	2.5	26.6	0.7
TS-1	Methanol	1	9.2	46.4	1.4	0.8	3.4	2.5	45.1	0.4
TS-1	Water[d]	1	8.2	15.1	1.8	—	—	3.1	76.6	3.4
TS-1	*tert*-butyl alcohol	1	4.8	45.5	3.3	0.8	0.4	14.4	34.5	1.1
TS-1	Acetone	1	22.8	7.2	0.3	—	0.2	0.6	0.3	91.4[e]
VS-1	Acetonitrile	1	nil[f]							
Si-1[g]	Acetonitrile	1	nil							
Blank[h]	Acetonitrile	1	nil							

[a] Reaction conditions: catalyst = 100 mg (Si/Ti = 45; Si/V = 80), aniline = 10 mmoles, solvent = 20 ml, reaction temperature = 273 K, reaction time = 5 h. [b] NSOB - nitrosobenzene, NB - nitrobenzene, OAP - *o*-aminophenol, PAP - *p*-aminophenol, AB - azo- and AXYB - azoxy-benzenes. [c] Mostly oxygenated with more than one functional group. [d] Products were extracted with acetonitrile. [e] Condensation (imine) and hydroxylated products. [f] No conversion. [g] Silica polymorph with MFI structure. [h] No catalyst used.

while the selectivity to azoxybenzene increased from 22.4 to 26.6%.

For comparison, under similar reaction conditions, aniline oxidation was carried out over other catalysts such as VS-1 and silicalite-1, and they were found to be inactive. A blank run (with no catalyst employed) gave no product. The unique catalytic activity of TS-1 is believed to stem from the presence of Ti^{4+} ions, which are isomorphously substituted into the framework of the MFI structure during hydrothermal synthesis.

Fig. 1 shows the selectivity of the oxidation of aniline over TS-1, as a function of temperature. It is well known that the temperature can influence the activity and the selectivity of the products formed. The oxidation of aniline over TS-1 was studied in the temperature range of 273–313 K. As the temperature is increased from 273 to 313 K, the conversion of aniline increased from 7.3 to 48.3 mol% but the selectivity shifted from nitrosobenzene to azoxybenzene. The conversions are 7.3 (at 273 K), 12.4 (at 283 K), 18.5 (at 293 K), 35.2 (at 303 K) and 48.3 mol% (at 313 K). It was found from the selectivities of the products formed that the ratio of nitrosobenzene to azoxybenzene depends on the reaction temperature; the ratios are 3.2 (at 273 K), 1.6 (at 283 K), 0.5 (at 293 K), 0.3 (at 303 K) and 0.1 (at 313 K). We have also conducted the oxidation of aniline at 263 K. While the selectivity to nitrosobenzene is increased to 85%, the conversion of aniline is around 3 mol%.

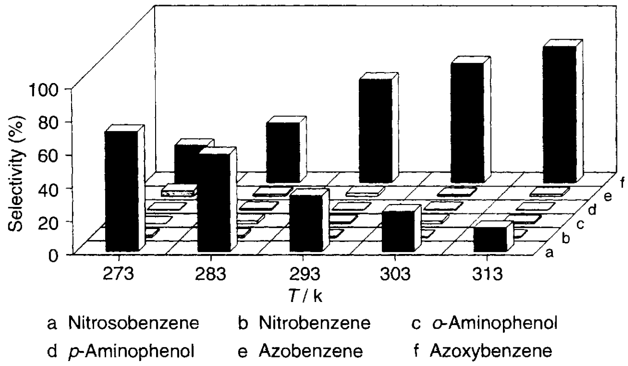

Fig. 1 Selectivities of the oxidation of aniline over TS-1, as a function of temperature. Reaction conditions: catalyst = 100 mg (TS-1, Si/Ti = 45), aniline = 10 mmoles, H_2O_2–aniline = 1 (mol ratio), solvent = 20 ml (acetonitrile) and reaction time = 5 h.

Azoxybenzene was not detected in the final product. This result suggests that most probably, the highly reactive nitrosobenzene might have been converted into azoxybenzene at higher temperatures either by the condensation of the primary intermediate, phenylhydroxylamine, with nitrosobenzene[18] or by the condensation of nitrosobenzene with unreacted aniline, which leads to the formation of azobenzene,[19] which is then further oxidized to azoxybenzene.[20]

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