Selective catalytic oxidation of aniline to azoxybenzene over titanium silicate molecular sieves

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The oxidation of aniline using aqueous H_2O_2 and titanium silicates, TS-1 and TS-2 as catalysts was carried out in a batch reactor in the temperature range 333–353 K. TS-1 catalyzes aniline selectively to azoxybenzene and is superior to TS-2. The influence of different solvents, concentration of H_2O_2 and the catalyst in the reaction mixture on the conversion and product distribution has been studied. Acetonitrile is a suitable solvent in this reaction, while acetone is not. For the TS-1 catalyzed oxidation reaction, *t*-butyl hydroperoxide is not a suitable oxidant. At optimum conditions, a H_2O_2 efficiency of about 100% for aniline conversion is obtained with a selectivity of 97% to azoxybenzene in the product.

Keywords: aniline oxidation; titanium silicates; selective oxidation of aniline; catalytic oxidation with H_2O_2; oxidation with TS-1 and TS-2

1. Introduction

The titanium silicate molecular sieves, TS-1 (with MFI structure) [1] and TS-2 (with MEL structure) [2] exhibit unique catalytic properties in a number of reactions such as the hydroxylation of phenol [1] and benzene [3], the epoxidation of olefins [4], the ammoximation of carbonyl compounds [5] and the oxyfunctionalization of alkanes [6,7], using aqueous H_2O_2 as oxidant. These are the first set of metallosilicate molecular sieves having shape-selective oxidation capability, which can be exploited in many organic chemical transformations. Oxidation of aniline and substituted anilines with a variety of reagents and catalysts (both in homogenous and heterogeneous media) is well documented [8–13]. Depending on the type of catalyst and/or the oxidant used, the product spectrum can be varied. Azobenzene is obtained using MnO_2 as stoichiometric oxidant [8]. Aqueous peracids oxidize aniline to azo- and azoxybenzenes [9], while anhydric peracids oxidize aniline to nitrobenzene [10]. Vanadium and molybdenum complexes [11] catalyze the oxidation of aniline to nitrobenzene in the presence of *t*-butyl hydroperoxide, whereas with some titanium complexes only azoxybenzenes are formed [12]. Tungsten oxide in the presence of hydrogen peroxide oxidizes aniline to nitroso- and azoxybenzenes [13]. The oxidation of aniline to either azoxybenzene or to nitrobenzene using $RuCl_3$ or quaternary ammonium chloride in the presence of hydrogen peroxide has been reported [14].

Recently, Sonawane et al. [15] have reported that titanium substituted silicalite-1 could be an excellent catalyst for the selective oxidation of aniline to azoxybenzene. This was the first report on the TS-1 catalyzed heterogeneous oxidation of aniline, but very few details about the reaction and the nature of the products formed are given. Results of our detailed investigation on the oxidation of aniline catalyzed by TS-1 and TS-2, and the influence of different reaction parameters on the conversion and selectivity are presented here. The oxidation of alkylamines and cyclohexylamine over TS-1 to give the corresponding oximes as the main products has been communicated by Reddy and Jacobs [16].

2. Experimental

Titanium silicate molecular sieves, TS-1 and TS-2 were synthesized hydrothermally according to the published procedures [1,2]. The samples were calcined in dry air for 16 h in order to remove the organic template. All chemicals used in the synthesis were from Aldrich. The chemical analysis of the samples revealed that the Si/Ti ratios were 35 and 80 in the case of two TS-1 samples and 74 in the case of TS-2. The particle size of TS-1 samples was uniform (SEM) and of approximately 0.3 μm in size, whereas uniform but bigger particles of 1–1.5 μm size were seen in the TS-2 sample. The samples were further characterized by XRD, IR and adsorption techniques. The physico chemical properties of the samples are given in table 1.

The recorded XRD patterns of TS-1 and TS-2 samples are in good agreement with the reported profiles of the corresponding Ti-free silicalite samples in all respects, indicating the formation of highly crystalline TS-1 and TS-2 materials. No amorphous material was present in the samples. The surface areas, micropore volumes and sorption capacities given in table 1 are indicative of the purity of the samples prepared.

The oxidation of aniline was carried out batchwise in a 100 ml round bottomed

Table 1
Physico chemical properties of titanium silicates

Sample	Si/Ti ratio		Yield (wt%)	Particle size (μm)	Surface area (m^2 g^{-1})	Micropore volume (ml g^{-1})	Cyclohexane adsorption (wt%) [a]
	gel	product					
TS-1	50	35	75–80	0.3	410	0.19	6.5
TS-1	100	80	70–75	0.3–0.5	389	0.19	6.0
TS-2	100	74	75–80	1–1.5	363	0.18	5.8

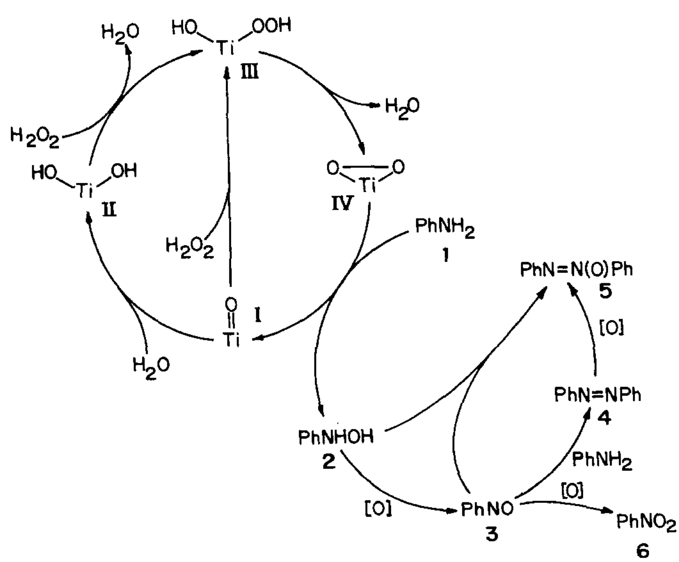
[a] Gravimetric (Cahn balance), temperature = 298 K, $p/p_0 = 0.5$.

flask with continuous stirring using mainly TS-1 as the catalyst. In a typical run, 0.25 g of the catalyst was dispersed in a solution containing 5 g of aniline (54 mmol) and 10 ml of a solvent. The mixture was vigorously stirred and 1.7 ml of H_2O_2 (30% aqueous solution) (18 mmol) was then added in one lot using a 5 ml graduated syringe as soon as the reaction temperature (333—353 K) was attained. After the completion of the reaction, the products were analyzed in a capillary gas chromatograph (HP 5890), fitted with a 50 ml long cross linked methyl silicone gum capillary column. The identity of the products was established by GC-MS (Shimadzu, QP 2000A). Conversions are given in terms of total amount of aniline converted to the initial concentration of aniline taken.

3. Results and discussion

3.1. THE REACTION PATHWAY

The oxidation pathways of aniline (shown in scheme 1) in presence of mono oxygen donors are well established [17]. As suggested by Huybrechts et al. [7], the titanium peroxo complex (IV) provides the reactive oxygen to convert aniline **1** into phenyl hydroxylamine **2** and subsequently to nitrosobenzene **3**. The formation of the phenyl hydroxylamine intermediate probably occurs within the TS-1 channels and as can be seen from the data of Sonawane et al. [15] on the oxidation of substituted anilines, the reaction is limited by the diffusion of the reactants and/or the primary products. Condensation of nitrosobenzene **3** with aniline **1** leads to the formation of



Scheme 1.

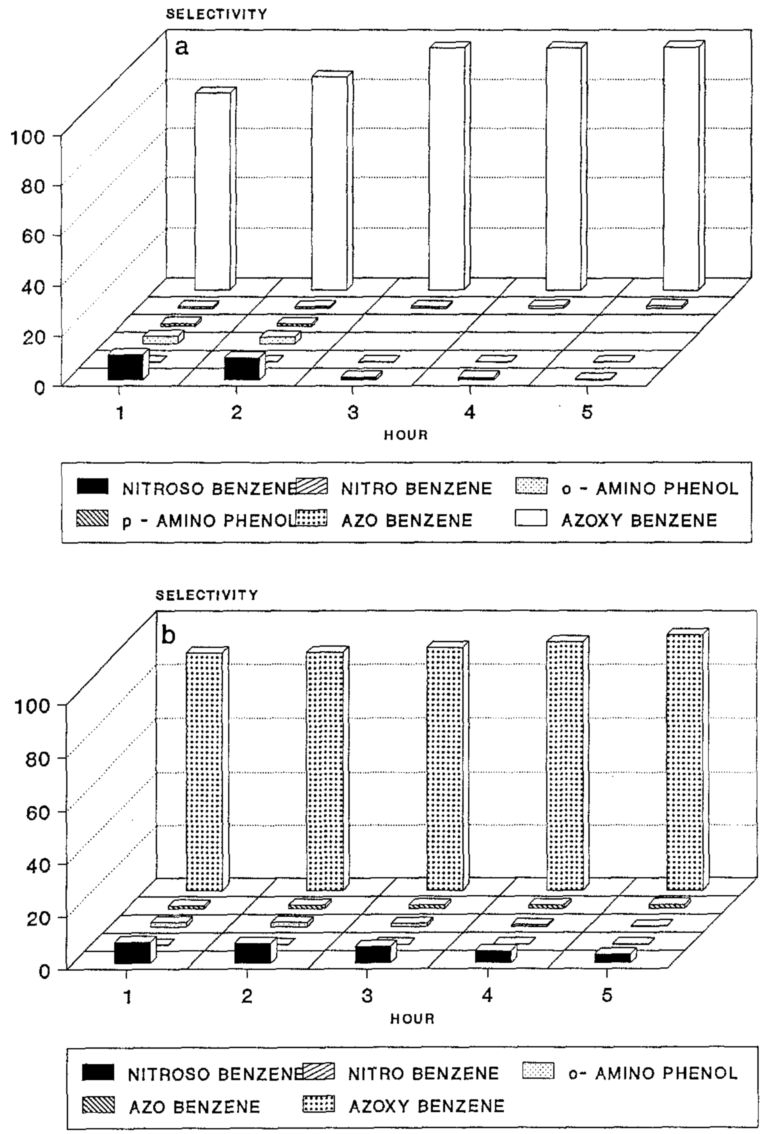


Fig. 1. Influence of mode of addition of H_2O_2 on the oxidation of aniline with TS-1. (a) Addition of H_2O_2 in one lot. (b) Addition over a period of 1 h. (c) Addition over a period of 5 h. (d) Aniline conversion and H_2O_2 selectivity for each mode of addition of H_2O_2 corresponding to (a), (b) and (c), respectively.

azobenzene **4** [18], which is further oxidized to azoxybenzene **5** [19] or is formed by the direct condensation of the two intermediates, phenyl hydroxylamine **2** and nitrosobenzene **3** [20]. Depending upon the initial concentration of H_2O_2, nitrobenzene **6** could also be a major product, but within the aniline/H_2O_2 mole ratios of 1–10 studied here, only traces of nitrobenzene are observed in the product.

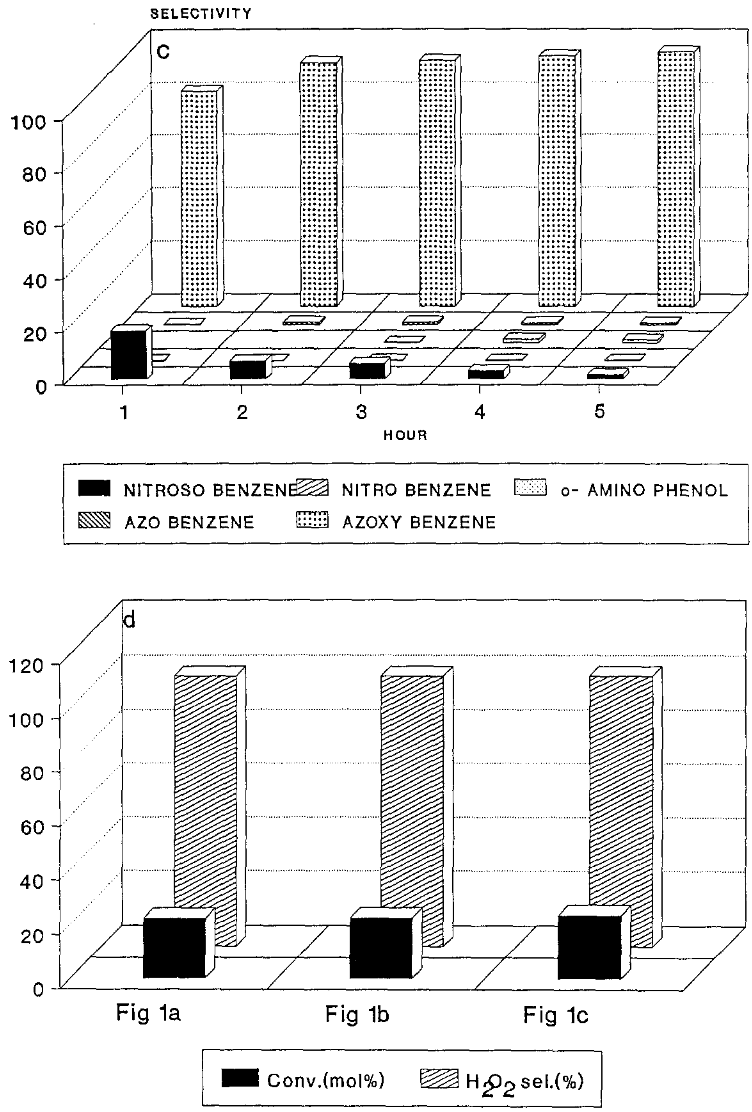


Fig. 1. (Continued.)

The major product at the end of 5 h reaction period is azoxybenzene, which is obtained with a selectivity invariably greater than 85%. Nitroso- and azobenzene intermediates and small quantities of nitrobenzene are identified and estimated in the final product of the reaction. Phenyl hydroxylamine was not detected in the product. The hydroxylation of the aromatic nucleus leads to the formation of aminophenols and titanium silicates are good catalysts in the hydroxylation of benzene, toluene and phenol under similar conditions. Only very small quantities of both *o*-aminophenol and *p*-aminophenol were found in the early stages of the reaction. However, in the final reaction/product mixture (after 5 h of run), the aminophenols were not detected. Presumably, the initially formed aminophenols were converted into high molecular weight tars, which are not detected in the GC analysis. Independent estimations have shown that the total tar content in the product did not exceed 2 wt%.

We will now discuss the various parameters on the above reaction.

3.2. THE MODE OF ADDITION OF H_2O_2

The mode of addition of H_2O_2 is an important factor determining the selectivity towards azoxybenzene and nitrosobenzene, since oxygen is consumed in two different stages of the overall oxidation reaction. Three different modes of H_2O_2 addition have been adopted: (i) addition of all the H_2O_2 in one lot in the beginning of the reaction (fig. 1a); (ii) addition of H_2O_2 over a period of 1 h (fig. 1b); and (iii) addition of H_2O_2 slowly over a period of 5 h (fig. 1c). The conversions obtained in the three cases are shown in fig. 1d.

In the initial stages of the reaction mixture, the concentration of nitrosobenzene was found to be quite high when compared to other products such as nitrobenzene, azobenzene, *o*- and *p*-aminophenols. Initially formed nitrosobenzene from phenyl hydroxylamine is more reactive and is immediately consumed in the formation of azobenzene by condensation with unreacted aniline and then converted into azoxybenzene. From the time-on-stream analysis of the products (fig. 1), the well established reaction scheme appears to hold well in this TS-1 catalyzed oxidation of aniline.

3.3. THE INFLUENCE OF DIFFERENT SOLVENTS

In many oxidation and hydroxylation reactions involving titanium silicate as catalyst, the solvent used in the batch reaction is known to influence the activity and the selectivity to the desired products [21,22]. Our results on the use of five different solvents of different polarities and dielectric constants in the oxidation of aniline are given in table 2. The reactions were carried out at 353 K, keeping aniline to the H_2O_2 mole ratio of 3 in the reaction mixture. The extent of conversion of aniline (upto 5 h of reaction duration) in different solvents is found to be in the order acetone > acetonitrile > methanol > *t*-butanol > water. However, the selectivity towards azoxybenzene in the product is found to be in the order *t*-butanol > water > acetonitrile > methanol > acetone. Methanol and *t*-butanol are reported to be suitable solvents in the synthesis of oximes from primary aliphatic amines on TS-1 [16]. In presence of acetone, primary amines and anilines are known to condense strongly forming corresponding imines ($Ph{-}N{=}CMe_2$ from aniline) [23]. The formation of imine and their hydroxylated products accounts for about 40% of the total products (table 2) when acetone is used as solvent and hence

Table 2
Effect of solvent, temperature and H_2O_2 concentration on aniline oxidation [a]

Aniline /H_2O_2 mole ratio	Temp. (K)	Solvent used	Conv. (mol%)	H_2O_2 sel. [b] (%)	Product distribution (%)				
					NSOB	NB	AB	AXYB	others [c]
3	353	CH_3OH	20.6	93.3	13.4	0.3	2.8	80.6	1.9
3	353	*t*-BUOH	15.2	69.6	0.2	1.8	0.6	97.3	0.1
3	353	H_2O [d]	14.3	65.7	0.5	2.3	0.4	96.7	0.1
3	353	CH_3COCH_3	24.8	66.7	5.7	0.2	0.9	51.2	39.6 [e]
3	353	CH_3CN	23.7	100.0	1.6	0.2	2.2	91.8	4.2
3	353 [f]	CH_3CN	19.1	82.4	4.8	–	1.3	88.1	5.8
3	343 [f]	CH_3CN	13.4	63.3	20.7	–	0.8	77.9	0.6
3	333 [f]	CH_3CN	9.8	50.8	21.8	–	0.3	75.7	2.2
1	333 [f]	CH_3CN	14.7	21.7	3.1	1.9	6.3	86.4	2.3
5	333 [f]	CH_3CN	7.3	57.8	24.6	–	4.3	71.1	–
10	333 [f]	CH_3CN	5.7	90.6	27.1	–	2.0	70.1	0.8

[a] Reaction conditions: aniline = 54 mmol, catalyst = 0.25 g (TS-1 (Si/Ti = 80)), reaction time = 5 h.
[b] H_2O_2 utilized in the formation of nitroso- (NSOB), nitro- (NB), azo- (AB) and azoxybenzenes (AXYB).
[c] Mostly oxygenated with more than one functional group.
[d] Products were extracted with benzene.
[e] Condensation (imine) and their hydroxylated products.
[f] Catalyst amount used in this study was 0.05 g.

the selectivity to azoxybenzene is considerably lower in acetone than in other solvents. This condensation reaction also occurs in the absence of any catalyst.

In methanol and in acetonitrile, the H_2O_2 selectivity is found to be in the order of 94–100%, whereas in *t*-butanol and water, it is at least about 25% lower. One notable feature is that the concentration of nitrosobenzene, is considerably higher (13.4%) in the product when methanol is used as solvent. The condensation reaction between nitrosobenzene and aniline leading to the formation of azobenzene is probably inhibited in methanol solvent. This is one of the reasons for the lower selectivity to azoxybenzene in this case. On the other hand, a selectivity of the order of 97% to azoxybenzene in both *t*-butanol and water is due to negligible by-product formation at an aniline conversion level of about 15 mol%. The amount of nitrobenzene, however, is found to be slightly higher in these two solvents.

3.4. THE INFLUENCE OF H_2O_2 CONCENTRATION

The results on the variation of aniline to H_2O_2 ratio in the reaction mixture are included in table 2. The data at 333 K show that as the concentration of H_2O_2 in the reaction mixture is increased, both conversion and selectivity to azoxybenzene increase. For maximum conversion and azoxybenzene formation, the aniline to

H_2O_2 (mole) ratio must be kept as low as possible. The azoxybenzene to nitrosobenzene ratio is also higher when the H_2O_2 concentration is more, the ratios being 27.8, 3.4, 2.8 and 2.5 at aniline to H_2O_2 ratio of 1, 3, 5 and 10, respectively (table 2). This indicates that the oxidation of azo- to azoxybenzene becomes more prominent than nitroso- to nitrobenzene as the H_2O_2 concentration in the reaction mixture is increased. In fact, at high concentration of H_2O_2 and with phase-transfer catalysts selective formation of nitrobenzene has been reported [14]. It is not clear at the moment as to why nitrobenzene formation is only a minor pathway in the oxidation of aniline with TS-1 as catalyst.

3.5. THE INFLUENCE OF TEMPERATURE

We have chosen acetonitrile as the solvent for studying the influence of temperature between 333 and 353 K on the conversion and selectivity in this reaction, while keeping the aniline to H_2O_2 mole ratio at 3 and the catalyst amount (g/moles of aniline) at 0.93 (0.05 g of catalyst). Our results are included in table 2. The reaction temperature has a positive influence on aniline conversion, which increases from 9.8 to 19.1 mol% between 333 and 353 K, respectively. The reaction rate increases from 2.9 to 5.8×10^{-7} mol cm^{-3} s^{-1} between these two temperatures. From the product distribution, it is seen that the azoxybenzene to nitrosobenzene ratio is dependent on the reaction temperature, the ratio being 3.4 at 333 K, 3.7 at 343 K and 18.3 at 353 K. At temperatures above 343 K, the condensation of nitrosobenzene with aniline is probably faster. Further oxidation of azobenzene to azoxybenzene is relatively less influenced by an increase in the reaction temperature. The selectivity to azoxybenzene, therefore, increases from 75.7% at 333 K to 88.1% at 353 K.

3.6. INFLUENCE OF TITANIUM CONTENT AND CATALYST CONCENTRATION

Table 3 reports the catalytic activity of TS-1 samples with two different Si/Ti ratios in the oxidation reaction, using acetonitrile as solvent. Both aniline conversion and H_2O_2 selectivity are marginally higher with high Ti-catalyst (Si/Ti = 35) but these are significantly higher than when the reaction was carried out with Ti-free silicalite-1 as catalyst. That TS-1 is active in this reaction is also clear from the blank experimental results given in table 3. It may be noted that in the blank experiments (one without catalyst and one with Ti-free silicalite-1) the selectivity to azoxybenzene is still the maximum. Presence of titanium and its content in the reaction mixture enhances the rate of oxidation of aniline to phenyl hydroxylamine and then to nitrosobenzene. When the amount of the catalyst is increased from 0.93 to 4.65 g per mole of aniline in the reaction mixture, both conversion and efficiency in the utilization of H_2O_2 increase from 9.8 to 21.8 mol% and 50.8 to 100%, respectively.

Table 3
Influence of titanium content and catalyst concentration on aniline oxidation [a]

Si/Ti ratio	Catalyst amount (g/mole of aniline)	Conv. (mol%)	H_2O_2 sel. (%)	Product distribution (%)				
				NSOB	NB	AB	AXYB	others
35	0.93	16.1	79.4	8.4	–	0.4	87.0	4.2
80	0.93	9.8	50.8	21.8	–	0.3	75.7	2.2
S-1 [b]	0.93	4.1	20.1	23.2	–	2.1	67.3	7.4
80	2.79	14.9	73.8	12.7	–	1.7	81.2	4.4
80	4.65	21.8	100.0	8.2	0.2	0.8	84.7	6.1
blank [c]	nil	2.8	14.4	26.1	–	9.8	63.0	1.1

[a] Reaction conditions: aniline = 54 mmol, aniline/H_2O_2 (mole ratio) = 3, reaction time = 5 h, solvent = acetonitrile (10 ml), temperature = 333 K.
[b] Titanium-free silicalite-1 sample, for comparison.
[c] No catalyst was used.

3.7. COMPARISON WITH TS-2 AND USE OF TBHP

A comparison of the activities of TS-1 and TS-2 in the oxidation of aniline using H_2O_2 or *t*-butyl hydroperoxide (TBHP, 70%) as oxidant is given in table 4. Both TS-1 and TS-2 catalysts having almost similar Si/Ti ratios were used. Between TS-1 and TS-2, the conversion and H_2O_2 selectivity are higher with TS-1 as catalyst and H_2O_2 as oxidant. The selectivity to azoxybenzene, however, is higher on TS-2 under similar conditions.

Although both TS-1 and TS-2 have similar pore dimensions and differ by the way the channels are interconnected, the H_2O_2 efficiency was only 82% on TS-2 in 5 h, whereas 100% H_2O_2 efficiency was achieved in about 2 h over TS-1. Differences in particle size or the morphology are known to influence the activity of TS-1 and TS-2 in phenol hydroxylation. The observed difference between TS-1 and TS-2 in our study (table 4) and also reported earlier by Sonawane et al. [15] could be due to the larger particle size of the TS-2.

Table 4
A comparison of TS-1 and TS-2 and influence of different peroxides [a]

Catalyst	Peroxide used	Conv. (mol%)	H_2O_2 sel. (%)	Product distribution (%)				
				NSOB	NB	AB	AXYB	others
TS-1	H_2O_2	23.7	100.0	1.6	0.2	2.2	91.8	4.2
TS-2	H_2O_2	17.9	81.9	1.2	1.1	0.3	97.2	0.2
TS-1	TBHP	5.9	19.7	7.5	1.5	3.0	59.7	28.3
TS-2	TBHP	1.3	4.9	12.1	2.9	16.2	52.7	16.1

[a] Reaction conditions: catalyst = 0.25 g (TS-1 (Si/Ti = 80), TS-2 (Si/Ti = 74), aniline = 54 mmol, aniline/H_2O_2 (mole ratio) = 3, temperature = 353 K, reaction time = 5 h.

The use of peracids and *t*-butyl hydroperoxide as oxidants in this oxidation reaction is extensive [8–14]. In our study, we have tried *t*-BuOOH in place of H_2O_2 as oxidant and found that both the conversion and the H_2O_2 selectivity are far lower when TBHP was used as the oxidant with either of the two titanium silicates (table 4). In fact, aniline conversion is negligible with TBHP on TS-2. Apparently, the formation of Ti-peroxo complex within the channels of the molecular sieve is inhibited due to size restriction of the *t*-BuOOH molecule. No C–H bond hydroxylation, for instance, took place on TS-1 when TBHP was used as the oxidant [24]. What is significant is that the selectivity to azoxybenzene is also greatly affected by the use of TBHP and non-selective oxidation reactions become important.

4. Conclusions

The titanium silicate molecular sieve TS-1 catalyzes the oxidation of aniline selectively to azoxybenzene with aqueous H_2O_2 as oxidant and is superior to TS-2. Lower aniline to H_2O_2 (mole) ratios, and higher catalyst concentrations in the reaction mixture are favourable for higher conversion and better H_2O_2 utilization. Acetonitrile is found to be a good solvent in this reaction. In presence of acetone, formation of imine and their hydroxylated products results in poor selectivity to azoxybenzene. A selectivity of the order of 97% to azoxybenzene could be achieved at 25 mol% conversion of aniline under certain reaction conditions. With *t*-butyl hydroperoxide as oxidant both conversion and selectivity to azoxybenzene are poor.

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