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Enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/H_2O_2 under solvent-free triphase conditions

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Abstract

A significant enhancement (3–10 times) in the reaction rates of the hydroxylation of aromatics (such as benzene, toluene and anisole), along with a reversal in regio-selectivity of the products of substituted benzenes such as toluene and anisole was achieved under solvent-free, triphase conditions (solid–liquid–liquid), catalyzed by TS-1 using dilute H_2O_2, compared to that obtained under conventionally used biphase conditions in the presence of a co-solvent (solid–liquid). While in the presence of a co-solvent (like acetone, acetonitrile or methanol) a long induction period was observed, in solvent-free conditions the induction period was almost absent. The effect of various reaction parameters such as substrate/H_2O_2 molar ratio, reaction temperature, catalyst concentration, stirring speed and the dilution level was also studied. In the case of substituted benzenes (anisole and toluene) *para*-hydroxy product was predominantly obtained under triphase conditions. However, in biphase the formation of *ortho*-isomer was preferred. Probable factors responsible for an enhancement in the activity and a change in regio-selectivity are:

1. relative hydrophobic nature and restricted pore dimensions of titanium silicate TS-1; and
2. diffusive resistance faced by the substrate with an organic co-solvent in biphase while such a resistance is minimized in triphase. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxylation; Regio-selectivity; Titanium silicate TS-1; Triphase-catalysis; Aromatics

1. Introduction

There is an increasing emphasis for developing new environmentally safer chemical transformations by reducing/removing the toxic waste where by-products from the chemical processes are avoided or minimized making them ecologically more acceptable [1–4]. It is highly desirable to develop eco-friendly methods for producing organic fine chemicals. One of the major problems encountered in various chemical processes is the use of organic solvents. Hence, the organic transformations under solvent-free conditions are attracting increasing attentions [3,4]. The use of large quantities of organic solvents is not only detrimental to environment but also economically unfavorable.

Crystalline microporous titanium–silicates [5–7] are extensively used as solid catalysts in oxidation of various organic substrates in the presence of dilute H_2O_2 and organic co-solvents [7–14]. However, the use of environmentally detrimental organic solvent creates problems in product separation and solvent recycle which are energy intensive steps. Hence, it is important to develop suitable methodology where the

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oxidation reactions catalyzed by TS-1 using H_2O_2 as an oxidant can be carried out in the absence of organic solvents, even if comparable conversion and selectivity, with respect to conventional processes, are achieved. The triphase conditions are expected to lead to easier work-up after the reaction.

Recently, we have shown, based on our preliminary studies, that TS-1 can efficiently be used under triphase conditions in the oxidation of water-immiscible organic substrates such as toluene, anisole, *m*-cresol, benzyl alcohol and cyclohexanol [8]. Quite interestingly, under such triphase conditions where no organic solvent was used (solid TS-1+water immiscible organic substrate+water+H_2O_2), a significant enhancement in activity (4–6 times) and *para*-selectivity was achieved [8].

Although the hydroxylation of phenol, catalyzed by TS-1 using H_2O_2 as an oxidant, has been studied extensively during the last one decade [5–7,9–11], very little is known about the hydroxylation of benzene [12,13], anisole and toluene [8,14]. Now, we report detailed studies using TS-1 as a very efficient catalyst for the oxidation of benzene, anisole and toluene under solvent-free, triphase conditions (solid catalyst, organic and aqueous phases). The results obtained in triphase conditions are compared with those obtained in conventionally employed biphase conditions using organic co-solvents.

2. Experimental

The catalyst TS-1 was synthesized employing our recently developed concept of promoter induced synthesis of zeolite materials [15] adapting the published recipe of TS-1 using Thangaraj procedure [6]. For synthesizing TS-1, first 42 g of tetraethyl-orthosilicate, TEOS (Aldrich) was added to 81.2 g of tetrapropyl-ammonium hydroxide solution, TPA–OH (ca. 20 wt% aq., Aldrich) under vigorous stirring for 1 h followed by slow addition of 2.24 g tetra-*n*-butyl-titanate, TNBT (Aldrich) taken in 9 g isopropyl alcohol, IPA, to clear TPA–silicate solution. Finally, a solution of 1.54 g H_3PO_4 (85% s.d. fine chem, India) in 9 g water was added and the stirring was continued for another 1 h. Clear solution, thus obtained, was autoclaved at 433 K for 6 h under agitation (60–62 rpm). The molar composition of the initial mixture was: 1.0 TEOS:0.033 TNBT:0.4 TPA–OH:0.75 IPA:0.067 H_3PO_4:25.0 H_2O. After crystallization, the solid was separated, washed thoroughly with deionized water, dried and calcined at 773 K for 16 h in an air flow. The calcined sample was treated with dilute H_2SO_4 solution (3 wt% aq.) at room temperature for 2 h and then centrifuged, washed thoroughly and dried. The TS-1 sample was characterized through well-known techniques such as XRD (Rigaku, D MAX III VC), SEM (JEOL, JSM 5200), FTIR (Nicolet 60 SXB spectrometer), UV–Vis (UV-2101 PC) and adsorption, to ascertain that the catalyst is free from amorphous and crystalline impurities.

The catalytic reactions were carried out in a glass-batch reactor. In a typical reaction, 0.1 mol of the substrate and x mmol of H_2O_2 (35 wt% aq.) were reacted over the catalyst in presence of water (under triphase) or an organic co-solvent (in biphase) under *vigorous stirring* (400–800 rpm). The substrate to water or substrate to co-solvent ratio (wt/wt) was kept constant to maintain the same dilution level of the reaction mixture in both the biphase and triphase systems. The additional water, apart from coming through aqueous H_2O_2, was taken for dispersion of the catalyst in this heterogeneous system and to maintain the dilution level. The products were collected and analyzed through high resolution gas chromatography (HP 5880) using flame ionization detector and a capillary column (HP 101 methyl silicone fluid, 50 m×0.2 mm with 0.2 μm thickness of coated film). In triphase, the two layers (organic and aqueous) of products were homogenized by adding acetone before analysis. Ocassionally, the organic and aqeous layers were separated, weighed and analyzed separately. In both ways, the GC results were comparable.

3. Results and discussion

3.1. Catalyst characterization

The XRD pattern of fully crystalline TS-1 sample was characteristic of MFI topology. The Si/Ti molar ratio in the solid was 32 as determined by chemical analysis (XRF). The scanning electron micrograph of TS-1 sample synthesized using promoter H_3PO_4, exhibits small crystallites (100–200 nm) with quite narrow particle size distribution. UV–Vis spectrum of TS-1

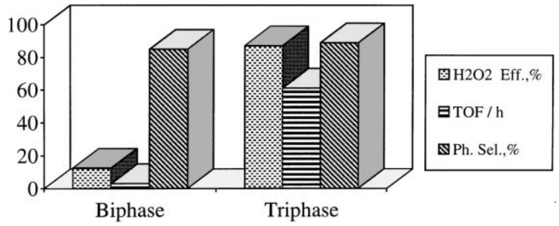

Fig. 1. Hydroxylation of benzene.

sample exhibited a sharp absorption at ca. 215 nm. The absence of any peak in the range 260–360 nm clearly indicated the absence of extra framework TiO_2 species [6–15].

3.2. *Hydroxylation of benzene*

Fig. 1 compares the results obtained in benzene hydroxylation under triphase and biphase conditions. In the presence of a co-solvent (biphase) the reaction was very slow and only ca. 12 mol% H_2O_2 efficiency could be obtained after 8 h. However, under presently used triphase condition, the reaction was very fast from the beginning itself reaching maximum conversion level (ca. 85 mol% H_2O_2 efficiency) in 2 h. Kinetic study showed that the selectivity for phenol also increases, at the expense of secondary products (*para*-benzoquinone, catechol and hydroquinone), with time. Since in this case the total amount of H_2O_2 was added in a lot at the beginning of the reaction, it is quite likely that secondary oxidation products are also formed at increased rate in the beginning. However, as the reaction proceeds, with the progressive utilization of oxidant, the relative formation of secondary products also decreased with time.

Table 1 shows the effect of substrate to H_2O_2 molar ratio in the hydroxylation of benzene under tri- and biphase conditions. By increasing the benzene/H_2O_2 molar ratio, both the H_2O_2 efficiency (utilization towards the formation of phenol, and its further oxidation products like *para*-benzoquinone, catechol and hydroquinone), and phenol selectivity among products were also increased, as expected. However, the benzene conversion and H_2O_2 efficiency towards hydroxy benzenes are considerably higher in triphase than that in the presence of organic co-solvent (biphase). The corresponding increase in reaction rate (TOF) was

Table 1
Effect of various benzene (Benz.) to H_2O_2 mole ratio on the oxidation of Benz. over TS-1 under triphase[a]

Benzene/H_2O_2 mole ratio	Phase[b]	Conversion (mol%)		H_2O_2 efficiency[c] (mol%)	TOF[d] (h^{-1} [c])	Phenol selectivity[e] (mol%)
		Experimental	Theoretical			
1.0	Tri	74.4	100	84.8	72.5	85.6
	Bi	11.6	100	13.7	2.9	82.0
1.5	Tri	52.3	66.7	86.2	49.1	89.5
	Bi	9.8	6.7	16.6	2.4	86.9
2.0	Tri	41.1	50.0	87.2	37.2	90.4
	Bi	8.7	50.0	19.2	2.1	90.1
3.0	Tri	28.8	33.3	90.5	25.5	95.0
	Bi	6.4	33.3	20.6	1.5	92.8

[a] Catalyst TS-1 (15 wt% with respect to substrate, H_2O_2 was slowly fed into the reaction mixture for a period of 30 min). Temperature 333 K, benzene:H_2O=1:5. Reaction time=2 h (triphase) and 8 h (biphase).

[b] In biphase acetonitrile was used as solvent, benzene:solvent=1:5 (wt/wt). Almost similar results were obtained when acetone or methanol was used as solvent in place of acetonitrile.

[c] Calculated considering the utilization of one mole H_2O_2 in the formation of phenol+two moles for the formation of catechol, hydroquinone and *para*-benzoquinone, and mol% H_2O_2 efficiency is based on the moles of H_2O_2 taken.

[d] Turn over frequency=moles of H_2O_2 converted for producing phenol+secondory products (catechol, hydroquinone and parabenzoquinone) per mole of Ti per hour.

[e] The rest of the products include *para*-benzoquinone, catechol and hydroquinone; orthobenzoquinone was not detected.

Table 2
Effect of temperature on the activity and selectivity in the oxidation of benzene over TS-1, under triphase

Temperature (K)	Benzene conversion (mol%)	H_2O_2 effeciency (mol%)	Time (h)[a]	TOF (h^{-1})	Phenol selectivity (mol%)
323	67.8	70.5	3.0	40.2	96.0
333	74.4	84.8	2.0	72.5	85.6
343	78.6	85.7	1.5	90.7	86.5
353	72.3	88.2	1.0	150.8	78.4

[a] Benzene:H_2O_2 mole ratio=1:1, other conditions are same as that given in Table 1.
[b] Time at which maximum benzene conversion was achieved.

about 15–25 times (Table 1). The benzene conversion, H_2O_2 efficiency, rate of reaction (TOF) and phenol selectivity increase with increasing the benzene to H_2O_2 molar ratio. Small amount of secondary oxidation products (10–20%), like *para*-benzoquinone, catechol and hydroquinone formed due to further hydroxylation of primarily formed phenol, was also obtained. In all other experiments, presented below, only triphase conditions were used.

The effect of the reaction temperature on the conversion and the phenol selectivity under triphase is shown in Table 2. By increasing the temperature from 323 to 353 K the rate of reaction (TOF) increases, along with the formation of secondary products, as expected. However, the optimum reaction temperature with respect to conversion, H_2O_2 efficiency and phenol selectivity, under present conditions, was found to be 333 K.

Table 3 illustrates the effect of the ratio of water to substrate (benzene, wt/wt) on the conversion and phenol selectivity. At water to benzene ratio=5:1, maintaining 15 wt% catalyst w.r.t. benzene (entry 5), maximum benzene conversion as well as optimum H_2O_2 efficiency were observed. Although increasing this ratio beyond 5 resulted in decreased benzene conversion and H_2O_2 efficiency, a decrease in the water to benzene ratio (wt/wt) resulted in progressive decrease of benzene conversion, H_2O_2 efficiency and phenol selectivity, indicating that at lower dilution secondary reactions (i.e. oxidation of phenol to catechol, hydroquinone and *para*-benzoquinone) are facilitated (entries 1–6). Although in these experiments the substrate to catalyst ratio (wt/wt) was same, the catalyst concentration with respect to total reaction volume was also changed considerably. Therefore in the next set of experiments, the effect of water to

Table 3
Effect of water/benzene (Benz.) ratio (wt/wt) on the conversion and phenol selectivity over TS-1 (temperature 333 K, H_2O_2 was added in a lot; reaction time=2 h)

Entry	H_2O:benzene (wt/wt)	Catalyst wt% w.r.t.		Conversion[a] (%)	H_2O_2 efficiency (%)	TOF (h^{-1})	Phenol[b] selectivity (%)
		Benzene	Total				
1	1.0	15	6.0	14.3	39.9	17.1	60.3
2	2.0	15	4.3	30.1	81.3	34.7	64.9
3	3.0	15	3.3	33.4	85.7	36.6	71.7
4	4.0	15	2.8	36.2	88.3	37.8	79.8
5	5.0	15	2.4	41.1	87.2	37.2	90.4
6	7.5	15	1.7	34.6	75.9	32.4	90.3
7	1.0	5.2	2.4	13.0	14.5	17.8	88.9
8	3.0	9.8	2.4	40.0	86.1	36.7	92.9
9	5.0	15	2.4	41.0	87.8	37.5	89.9

[a] Benzene:H_2O_2=2:1 (mol/mol).
[b] The rest were secondary products like *para*-benzoquinone, catechol and hydroquinone.

benzene weight ratio was also studied keeping the catalyst concentration in the total reaction volume constant (at different benzene/catalyst ratio). These results (Table 3, entries 5, 7–9), suggest that an optimum catalyst concentration with respect to both the substrate as well as the total reaction mixture is needed for achieving high phenol yields (i.e. high H_2O_2 efficiency and phenol selectivity).

3.3. *Hydroxylation of substituted benzenes (anisole and toluene)*

In Fig. 2, the results obtained in the hydroxylation of anisole under tri- and bi-phase are compared. In this case also the conversion, TOF and selectivity for 4-hydroxy anisole (*para*-isomer) were significantly enhanced under solvent-free triphase conditions compared to that obtained under biphase using organic solvent.

Table 4 discusses the effect of solvent on the hydroxylation of anisole over TS-1/H_2O_2 system. When H_2O was used as a dispersion medium (i.e. under triphase), *p*-isomer is the major product. Again, when co-solvent (like methanol, acetonitrile, etc.) is used then *o*-isomer is the major product. This is due to the fact that under triphase condition, the reaction occurs mainly inside the channels of TS-1, whereas under biphase condition the active sites present on the external surface are responsible for the reaction.

Table 5 deals with the effect of catalyst concentration on the hydroxylation of anisole under solvent-free triphase conditions with TS-1/H_2O_2 system. It is clear from the data given in Table 5 that maximum H_2O_2 efficiency is obtained when the catalyst concentration is ca. 20 wt% with respect to the substrate. This may be due to the fact that with increasing catalyst concentration, the number of active titanium species increases and hence increased conversion with more efficient utilization of the oxidant is obtained.

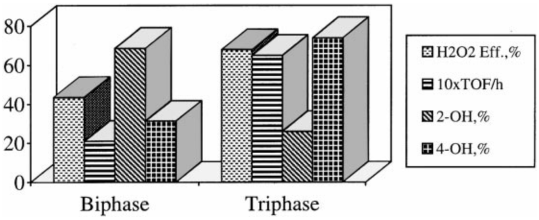

Fig. 2. Hydroxylation of anisole.

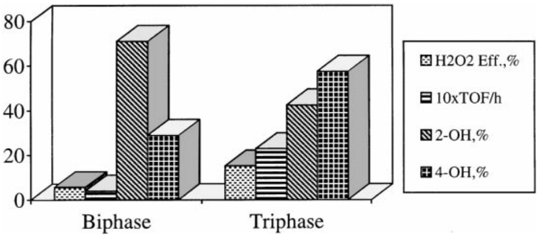

Fig. 3. Hydroxylation of toluene.

In the case of toluene also, the conversion and TOF in triphase were higher than that obtained in biphase (Fig. 3). Quite interestingly, like in the case of anisole, here also the regio-selectivity in the *para*- and *ortho*-hydroxy products (cresols) in the hydroxylation of toluene was completely reversed under tri- and biphases (Fig. 3). While, the ratio of *p*-cresol to *o*-cresol in tri- and bi-phases was 1.35 and 0.41, respectively (Fig. 3), in the case of hydroxy anisoles, the corresponding values for *para* to *ortho* ratio under tri- and bi-phases were 2.8 and 0.45, respectively (Fig. 2).

Since the microporous zeolites and related molecular sieves possess restricted pore dimensions and channel structure, bulkiness of the products plays an important role of monitoring the shape selective product-distribution. Significantly higher activity as well

Table 4
Effect of solvent on hydroxylation of anisole over TS-1/H_2O_2 system under triphase conditions (anisole:H_2O_2=5:1, anisole:solvent=1:5, catalyst concentration (w.r.t. anisole)=20 wt%, temperature=353 K)

Solvents	Conversion (mol%)	H_2O_2 efficiency (mol%)	Product distribution (mol%)	
			Ortho	*Para*
Acetonitrile	7.5	37.5	55	45
Methanol	9.0	45.0	60	40
Water	17.5	87.5	25	75

Table 5
Effect of catalyst concentration on the hydroxylation of anisole under solvent free triphase conditions with TS-1/H_2O_2 system (anisole:H_2O_2=5:1, anisole:water=1:5, temperature=353 K)

Catalyst concentration (wt%)	Conversion (mol%)	H_2O_2 efficiency (mol%)	Product distribution (mol%)	
			Ortho	*Para*
0	0.0	–	–	–
5	8.0	40	38	62
10	10.0	50	34	66
20	17.5	87.5	25	75

as high *para*-selectivity (in the case of substituted benzenes) obtained in the present triphase system indicate that the reaction may be occurring predominantly inside the zeolite channels. However, in the biphase system, low conversion as well as high *ortho*-selectivity (in the case of substituted benzenes like toluene, anisole) probably indicate that the reaction takes place significantly on the external surface of the catalyst as well.

Earlier also a reversal of regio isomers in the hydroxylation of phenol [14,16] and substituted benzenes such as toluene and anisole [14] was observed when different solvents (acetone and methanol) were used. Generally, acetone gave higher *ortho*-product while methanol favored the formation of *para*-isomer. This was attributed to the lower solubility of tar (mainly in the case of phenol hydroxylation) in methanol and thereby poisoning the external sites due to deposition of tar. Since tar is negligibly soluble in water, higher *para*-selectivity, observed in present triphase condition, may also be due to the selective poisoning of the catalytic sites on the external surface of the catalyst particles.

In relatively hydrofobic high silica titanium silicate molecular sieves, organic substrates are expected to be competing more favorably with water (vis-à-vis with organic solvent in biphase) for diffusion and adsorption inside the zeolite channels under triphase condition which is free from organic solvent. When an organic solvent is present along with the reactant, the diffusion and adsorption of the reactant will be hindered by the solvent. If it is true, then it may explain higher activity in triphase compared to that in biphase. To confirm this hypothesis some competitive adsorption experiments under bi- and tri-phase conditions (except the presence of H_2O_2) were carried out.

The FTIR spectra of various TS-1 samples used in the competitive experiments, TS-1/acetonitrile/benzene sample, showed [13] a doublet at ca. 2350–2360 cm^{-1} (characteristic peaks of acetonitrile in non-overlapping range with TS-1 vibrations), while TS-1/H_2O/benzene sample shows major peaks at 3060–3120 cm^{-1} and 1480 cm^{-1}, corresponding to benzene. It is quite clear from these results that benzene is main adsorbate under triphase while acetonitrile is mainly adsorbed in biphasic condition. This fact was also verified by desorption experiments [13]. Thermogravimetric analysis of adsorbed components in TS-1 after competitive adsorption in the case of anisole also supported the above results. TS-1, adsorbed with only anisole, gave a weight loss of 11.7% in the temperature range between 363 and 573 K. When TS-1 was adsorbed with anisole in presence of water, the TGA curve again exhibited a weight loss of ~12% in the same temperature range. Thus in presence of water it is anisole which is the main adsorbate. TS-1 sample adsorbed with water gave a weight loss of only ~2% in the range 313–423 K. However, when anisole and acetonitrile were coadsorbed in TS-1, it was acetonitrile (3.7 wt% at 313–363 K and 7.8 wt% at 363–523 K to be compared with 3.9 wt% at 313–363 K and 8.1 wt% at 363–523 K for TS-1/acetonitrile system), which was found to be mainly adsorbed in TS-1.

Although the above-mentioned explanation in triphase conditions may be accepted as far as the adsorption and diffusion of reactants inside the TS-1 channels (intra-particle diffusion) are concerned, the transport of reactant (benzene) to the solid surface through aqueous phase (external mass transfer) poses additional problem. Recently, Desikan and Doraiswamy [17] have reviewed this diffusion–reaction problem in triphase catalysis dealing with polymersupported phase transfer catalysts in various types of triphase catalytic systems, including solid–liquid–liquid (S–L–L) type. In any such S–L–L systems the overall activity depends on

1. external mass transfer,
2. intra-particle diffusion, and
3. intrinsic reactivity of the catalytic sites.

Although the last two phenomena are unique to TS-1 (molecular sieves) and are already discussed above in the present case of triphase catalysis over TS-1/H_2O_2 system, the external mass transfer is a common and probably most complicated problem in triphase catalysis in general [17].

In triphase conditions, the vigorous stirring needed for the reaction to occur (external mass transfer) helps the dispersion of organic phase in aqueous one through micro droplet formation and there by expected to facilitate the transport of the reactant to the catalyst surface. The stirring rate has a marked influence on the rate of reaction. Although, a detailed treatment of chemical engineering and theoretical aspects of this interesting phenomenon are obviously beyond the scope of the present communication we have tried to interpret the interesting results on the basis of the present work.

4. Conclusions

Compared to conventionally used biphase (solid catalyst+one homogeneous liquid phase, solid–liquid) conditions in TS-1/H_2O_2 system, the use of triphase (solid catalyst+two immiscible liquid phases, solid–liquid–liquid) solvent-free conditions results in

1. significant enhancement in the reaction rates in the hydroxylation of water immiscible aromatic compounds like benzene, anisole and toluene, and
2. high *para*-selectivity (in fact reversal of regio-selectivity) in the case of substituted benzenes.

The probable factors responsible for enhancement in activity and change in regio-selectivity are:

1. relative hydrophobic nature and restricted pore dimensions of titanium silicate TS-1,
2. diffusive resistance faced by the substrate with an organic co-solvent in biphase while such a resistance is minimized in triphase, and
3. in biphase, vis-à-vis triphase, external surface sites contribute to a larger extent.

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