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Triphase Catalysis over Titanium–Silicate Molecular Sieves under Solvent-free Conditions

I. Direct Hydroxylation of Benzene

Asim Bhaumik, Priyabrata Mukherjee, and Rajiv Kumar[1]

Catalysis Division, National Chemical Laboratory, Pune-411 008, India

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Under solvent-free triphase conditions (solid catalyst TS-1, organic substrate and aqueous H_2O_2, S-L-L) a significant enhancement in the reaction rate (ca by 15–25 times) during the oxidation of benzene, compared to that obtained under conventional biphase system using an organic solvent (solid TS-1 catalyst in the presence of a cosolvent to homogenize the organic and aqueous layers, S-L), was observed. Time-dependent studies in the hydroxylation of benzene over TS-1/H_2O_2 system indicated that while in the presence of a cosolvent (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 benzene/H_2O_2 molar ratio, mode of addition of H_2O_2, reaction temperature, catalyst concentration, stirring speed, and the dilution level on benzene conversion and phenol selectivity was also studied. Around 85 ± 5 mol% H_2O_2 utilization for oxygenated benzene products (reaction time = 2 h) as well as phenol selectivity could be obtained under the present solvent-free, triphase conditions (at 333 K and benzene to H_2O_2 mole ratio = 1–3). The corresponding values under similar reaction conditions, except the presence of organic solvent (reaction time = 8 h), in conventionally used biphase system were 17 ± 3 and 85 ± 5, respectively. Further, the present solvent-free method offers distinct advantages of easier workup and being environmentally safer, because of the absence of organic solvents. Competitive adsorption experiments suggest that under triphase condition benzene competes favorably with water for diffusion inside the TS-1 channels. However, under biphase conditions benzene faces strong competition with organic solvents for diffusion inside relatively hydrophobic TS-1 channels resulting in low conversion. © 1998 Academic Press

INTRODUCTION

One of the major problems encountered in catalytic, liquid phase organic transformations is the interaction between mutually immiscible reagent(s) and substrate (1). Under heterogeneous conditions (organic phase–aqueous phase reaction) the observed reaction rates are very slow, owing to the low concentration of at least one of the reactants in each phase. To overcome this problem cosolvents are generally used to bring about a homogeneous state and thereby completely eliminate the phase boundaries. Although, the use of cosolvents often finds its utility, product separation suffers from the drawback of complex workup procedure. Phase-transfer catalysts (2–4), used to overcome this problem, also suffer from the drawback that the catalyst used promotes the formation of emulsions, giving rise to severe problems in recycling and workup. Tetraalkylammonium cation supported resins (5, 6) and aluminas (7) have also been reported to be efficient triphase catalysts (solid catalyst resides at the interface of two liquid layers) in certain organic transformations.

During the last decade crystalline, microporous titanium silicate, TS-1 (8, 9), has been extensively used in oxidation of various organic substrates in the presence of dilute H_2O_2 using cosolvents (10–13). However, the use of environmentally detrimental organic solvent creates problems related to product separation and solvent recycle, which are energy intensive steps. Hence, it is desirable to develop suitable methodology, where the oxidation reactions catalyzed by the TS-1/H_2O_2 system could be carried out without using organic solvents so that the whole process becomes environmentally favorable, even if comparable conversion and selectivity, with respect to conventional processes, are obtained.

Recently, we have reported that TS-1 can efficiently be used under triphase conditions in the oxidation of water-immiscible organic substrates, such as toluene, anisole, m-cresol, benzylalcohol, and cyclohexanol (14). Quite interestingly, under 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 (14).

Although, phenol hydroxylation catalyzed by TS-1/H_2O_2 system has been extensively studied (8–12), very little is

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[1] Corresponding author. E-mail: rajiv@ems.ncl.res.in.

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known about benzene hydroxylation (13). Here, we report, for the first time, detailed studies using TS-1 as a very efficient catalyst for the oxidation of benzene under solvent-free, triphase conditions (solid catalyst, organic, and aqueous phases) with significant enhancement in the activity over conventional biphase system.

EXPERIMENTAL

The catalyst TS-1 was synthesized employing our recently developed concept of promoter induced synthesis of zeolite materials (15). For synthesizing TS-1 (9, 15), first 42 g of tetraethyl orthosilicate, TEOS (Aldrich), were added to 81.2 g of tetrapropylammonium hydroxide solution, TPA-OH (ca 20 wt% aq., Aldrich) under vigorous stirring for 1 h. Then 2.24 g of tetra-*n*-butyl titanate, TNBT (Aldrich), in 9 g isopropyl alcohol, IPA, were added very slowly into the clear silicate solution followed by the addition of a solution of 1.54 g H_3PO_4 (85% s.d. fine chem, India) in 9 g of water and the stirring was continued for another 1 h. The 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. This 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 impurities.

The liquid phase catalytic reactions were conducted 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., $x = 30$, 50, 67, and 100) were reacted over the catalyst in the presence of water (under triphase) or acetonitrile as cosolvent (in biphase) under *vigorous stirring* (ca 800 rpm). For comparison, two sets of experiments, one in biphase system in the presence of acetonitrile (commonly used solvent in TS-1/H_2O_2 catalysis) and the other in solvent-free triphase system, were carried out under identical conditions. The substrate to water or substrate to cosolvent ratio (wt/wt) was kept constant to maintain the same dilution level of the reaction mixture in both biphase and triphase systems. The additional water, apart from coming through aqueous H_2O_2, was used for dispersion of the catalyst in this heterogeneous system and to maintain the dilution level. Generally, H_2O_2 (35%) was slowly injected drop-wise using a syringe pump (Sega, USA) during 30 min, unless stated otherwise. The products were collected at various intervals of reaction times and were analyzed by high resolution capillary gas chromatography (HP 5880, using Flame Ionization Detector). The H_2O_2 selectivity is defined as the moles of H_2O_2 consumed in the formation of oxygenated benzene products and the phenol selectivity is defined as the of moles of phenol obtained among the total moles of oxygenated benzene products formed in the reaction.

For competitive adsorption experiments water was used for the dispersion of the catalyst under triphase condition, whereas acetonotrile was used instead of water in the case of biphase system maintaining the same conditions as employed during typical reaction, except the presence of H_2O_2; 7.5 g calcined TS-1 sample was taken in a 500-ml round bottom flask and 50-g benzene was fed into it followed by the addition of 250-g water. The mixture was then stirred with the help of a magnetic stirrer at 333 K for 2 h. The TS-1/water/benzene sample (sample B) was then filtered, dried in air at room temperature, and finally stored in a dessicator. The same sequence was followed during the competitive adsorption experiment under biphase system except that acetonitrile was used instead of water (TS-1/acetonotrile/benzene sample (sample C). The adsorbed TS-1 samples along with pure TS-1 (sample A) were characterized for the adsorbed materials by IR spectroscopy using KBr pellet technique. For desorption experiments, 5 g sample B or C was loaded in a tubular downflow glass reactor and then flushed with dry nitrogen at 523 K for 1 h. The desorbed material was cooled (in a liquid nitrogen trap), collected, and analyzed by gas chromatography using thermal conductivity (for sample B) or flame ionization (for sample C) detectors.

RESULTS

The XRD pattern of the 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). Figure 1 depicts the scanning electron micrograph of the TS-1 sample synthesized using promoter H_3PO_4, clearly showing that small crystallites (100–200 nm) with very narrow particle size distribution are obtained. Figure 2 depicts the UV-Vis spectrum of the TS-1 sample exhibiting a sharp absorption at ca 215 nm. The absence of any peak in the range of 260–360 nm clearly indicates the absence of extra frame work TiO_2 species (9–13).

Figure 3 depicts the effect of stirring speed on the conversion and phenol selectivity. These experiments were conducted in a stainless steel Parr autoclave (Parr, USA). Under triphase the conversion and phenol selectivity increase with the stirring speed upto ca 400 rpm before leveling off. The effect of stirring was rather pronounced in triphase system. By contrast, in biphase conditions no significant change in the conversion was observed under mild (200–300 rpm) and vigorous (400–800 rpm) stirring. For further experiments simple glass batch reactor with magnetic

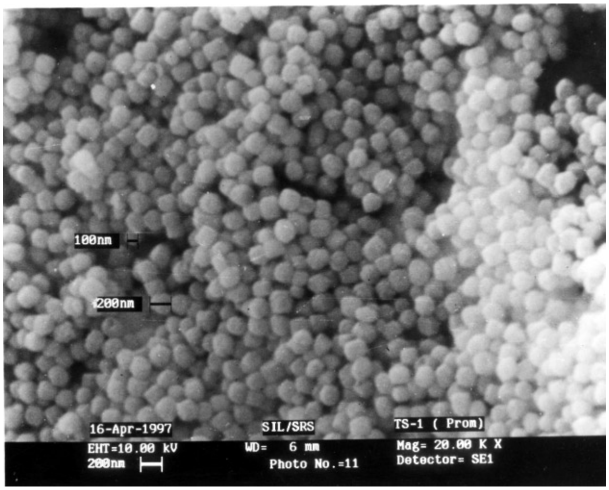

FIG. 1. Scanning electron micrograph of TS-1 sample.

stirring (ca 800 rpm) was used as the results obtained using Parr autoclave and the glass batch reactor, under otherwise same condition, were comparable.

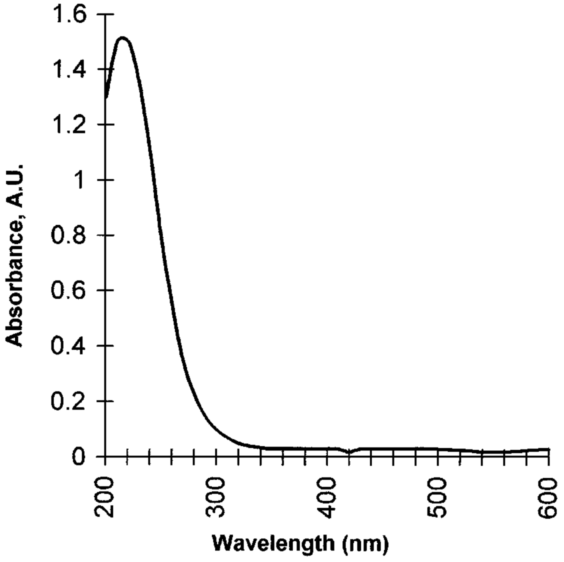

FIG. 2. UV-Vis spectrum of calcined TS-1 sample.

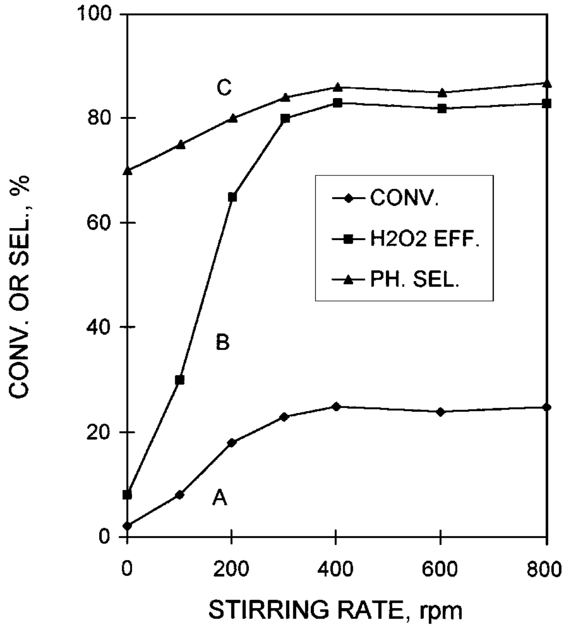

FIG. 3. Effect of stirring (rpm) on the conversion of benzene, H_2O_2 selectivity, and phenol selectivity (mol%) under triphase. Curves A, benzene conversion; B, H_2O_2 selectivity, and C, phenol selectivity. Benzene = 0.1 mole, H_2O_2 = 0.033 mole, catalyst = 1.17 g, and H_2O = 39 g (including that from 35 wt% H_2O_2). Reaction was carried out in a stainless steel Parr (USA) autoclave. Temperature = 333 K.

In Table 1, the effect of the substrate to H_2O_2 molar ratio in the hydroxylation of benzene over TS-1/H_2O_2 system under tri- and bi-phase conditions is reported. With increasing benzene/H_2O_2 molar ratio, both the H_2O_2 selectivity (utilization towards the formation of phenol, and its further oxidation products like *p*-benzoquinone, catechol, and hydroquinone) and phenol selectivity among products were also increased, as expected. However, the benzene conversion and H_2O_2 selectivity towards oxygenated benzenes are considerably higher (4–6 times) in triphase than could be achieved in the presence of organic cosolvent (biphase). The corresponding increase in reaction rate (T.O.F.) is about 15–25 times (Table 1). The benzene conversion, H_2O_2 selectivity, rate of reaction (TOF), and phenol selectivity increase by increasing benzene to H_2O_2 molar ratio. A small amount of secondary oxidation products (10–20%) like *p*-benzoquinone, catechol, and hydroquinone formed due to further hydroxylation of primarily formed phenol, were also obtained. In all other experiments, mentioned below, only triphase conditions were used.

In Fig. 4, the benzene conversion, H_2O_2 selectivity, and phenol selectivity are plotted as a function of reaction time under triphase conditions. In the presence of cosolvent the reaction was very slow and only ca 20% H_2O_2 selectivity could be obtained after 8 h (not plotted in Fig. 4). However, under the presently used triphase conditions, the reaction was very fast from the beginning, reaching maximum conversion level (ca 85% H_2O_2 selectivity) in 2 h. The selectivity for phenol also increases (curve B), at the expense of secondary products (curve C: *p*-benzoquinone, catechol, and hydroquinone), with time (Fig. 4). Since in this case the total amount of H_2O_2 was added in one lot at the beginning of the reaction, it is quite likely that secondary oxidation products are also formed at an increased rate in the beginning. However, as the reaction proceeds, with the progressive utilization of oxidant, the relative formation of secondary products also decreases with time.

In Table 2 the effect of temperature on the conversion and product selectivity in the hydroxylation of benzene

TABLE 1

Effect of Various Benzene to H_2O_2 Molar Ratios on the Oxidation of Benzene over TS-1 under Triphase[a]

Benz/H_2O_2 molar ratio	Phase[b]	Conv. (%) Exp.	Conv. (%) Theo.	H_2O_2 sel. (%)[c]	TOF[d] (h^{-1})	Product selectivity, %[e] PH	PBQ	CA	HQ
1.0	Tri	74.4	100	84.8	72.5	85.6	9.3	2.0	3.1
	Bi	11.6	100	13.7	2.9	82.0	10.4	4.6	3.0
1.5	Tri	52.3	66.7	86.2	49.1	89.5	7.5	1.2	1.8
	Bi	9.8	66.7	16.6	2.4	86.9	9.0	2.5	1.6
2.0	Tri	41.1	50.0	87.2	37.2	90.4	6.1	1.4	2.1
	Bi	8.7	50.0	19.2	2.1	90.1	6.0	2.3	1.6
3.0	Tri	28.8	33.3	90.5	25.5	95.0	2.9	2.8	1.3
	Bi	6.4	33.3	20.6	1.5	92.8	4.9	1.4	0.9

[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 : $H_2O = 1:5$ (wt/wt). 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 *p*-benzoquinone, and mole% H_2O_2 selectivity is based on the mole of H_2O_2 used.

[d] Turn over frequency = moles of H_2O_2 converted for producing phenol + secondary products (catechol, hydroquinone, and *p*-benzoquinone) per mole of Ti per h.

[e] PH = phenol, PBQ = *p*-benzoquinone, CA = catechol, and HQ = hydroquinone.

under solvent-free triphase is shown. Upon increasing the temperature from 323 to 353 K, the rate of reaction (T.O.F.) increases along with the formation of secondary products, as expected. However, the optimum reaction temperature, under the present conditions, was found to be 333 K. Hence, all other experiments were carried out at 333 K.

Table 3 illustrates the effect of continuous addition of H_2O_2 on the conversion and selectivity in the oxidation of benzene under triphase conditions. High H_2O_2 utilization for the oxygenated benzene products could be achieved from the beginning if the oxidant is added slowly. Table 3 also shows the amount of H_2O_2 added after different intervals of time. Here also, phenol selectivity increases slightly with time at the initial stages of the reaction at the cost of secondary oxidation products.

In Table 4, the effect of catalyst concentration on benzene hydroxylation is reported. Increasing the catalyst concentration (with respect to benzene) resulted in an increase in H_2O_2 utilization initially before leveling off at ca 85 ± 5%. Based on these results, ca 12.5–15 wt% catalyst with respect

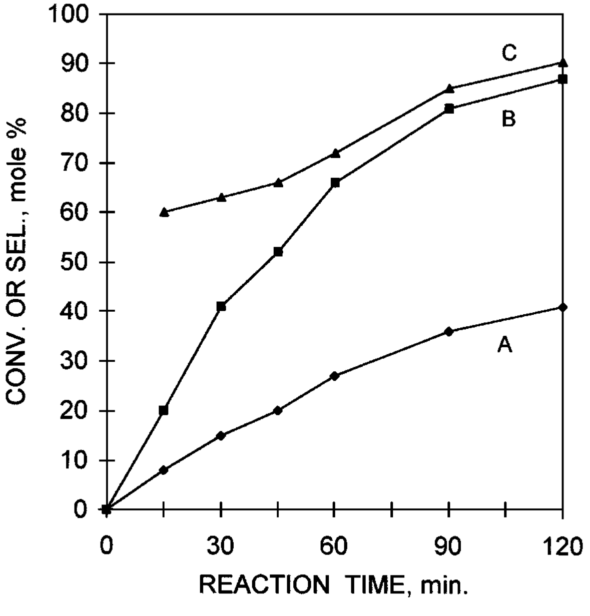

FIG. 4. Conversion and phenol selectivity as a function of reaction time in benzene hydroxylation catalyzed by TS-1/H_2O_2 system under triphase conditions. Reaction conditions: Temperature 333 K, catalyst TS-1 (15 wt% with respect to benzene), H_2O : benzene = 5 : 1 (wt/wt), benzene : H_2O_2 = 2 : 1 (mole/mole); A, benzene conversion; B, H_2O_2 efficiency; and C, phenol selectivity among oxidized products.

TABLE 2

Effect of Reaction Temperature on the Activity and Selectivity in the Oxidation of Benzene under Triphase

Temp. (K)	Benzene conv. (%)	H_2O_2 sel. (%)[a]	Time (h)[b]	TOF (h^{-1})	Product selectivity (%) PH	PBQ	CA	HQ
323	67.8	70.5	3.0	40.2	96.0	4.0	—	—
333	74.4	84.8	2.0	72.5	85.6	9.3	2.0	3.1
343	78.6	85.7	1.5	90.7	86.5	8.7	2.0	2.8
353	72.3	88.2	1.0	150.8	78.4	14.2	3.0	4.4

[a] Benzene : H_2O_2 molar ratio = 1 : 1, other conditions are same as that given in Table 1.

[b] Time at which maximum benzene conversion was achieved.

TABLE 3

Effect of Continuous Addition of H_2O_2 on the Conversion and Selectivity in the Oxidation of Benzene under Triphase[a]

Reaction time (min)	15	30	45	60	90	120
H_2O_2 added (mol% benzene)	12.5	25.0	37.5	50.0	75.0	100.0
Benzene conv. (%)	9.1	19.0	30.3	41.0	63.0	80.8
H_2O_2 sel. (%)[b]	91.0	92.7	92.5	92.3	91.1	91.3
Products, mol%						
Phenol, PH	75.0	79.8	84.6	87.4	91.6	88.6
p-Benzoquinone, PBQ	25.0	18.0	12.1	9.0	5.1	7.4
Catechol, CA	—	1.4	1.3	1.8	1.3	2.0
Hydroquinone, HQ	—	0.8	2.0	2.8	2.0	3.0

[a] Reaction conditions: Temperature 333 K, catalyst TS-1 (15 wt% with respect to benzene), H_2O : benzene = 5 : 1 (mass/mass), benzene : H_2O_2 = 1 : 1 (mole/mole).

[b] Conversion of H_2O_2 with respect to the moles of H_2O_2 added at that reaction time.

TABLE 4

Effect of Catalyst Concentration on Benzene Conversion and Product Selectivities

Catalyst conc., wt%[a]	Conv. (%)[b]	H_2O_2 sel. mole%	TOF (h^{-1})	Time (h)	Products, mol%			
					PH	PBQ	CA	HQ
5.0	26.8	58.6	37.6	4.0	90.8	9.2	—	—
10.0	37.3	84.7	36.2	3.0	86.4	11.1	1.1	1.4
12.5	38.1	87.6	36.0	2.5	85.0	12.7	1.0	1.3
15.0	41.1	87.2	37.2	2.0	90.4	6.1	1.4	2.1
20.0	33.6	90.3	38.6	1.5	65.7	19.4	6.0	8.9

[a] Catalyst TS-1 in wt% with respect to the substrate.

[b] Benzene : H_2O_2 molar ratio = 2 : 1 (maximum theoretical benzene conversion = 50%); other conditions are same as Table 1.

TABLE 5

Effect of Water Concentration on Conversion and Phenol Selectivity over TS-1/H_2O_2 : Temp. 333 K, H_2O_2 was Added in One Lot; Reaction Time = 2 h

Entry	H_2O : Benz. (wt/wt)	Catalyst wt%, w.r.t.		Conv.[a] (%)	H_2O_2 sel. (%)	T.O.F. (h^{-1})	Product selectivity, %			
		Benz.	Total				PH	PBQ	CA	HQ
1	1.0	15	6.0	14.3	39.9	17.1	60.3	24.0	6.3	9.4
2	2.0	15	4.3	30.1	81.3	34.7	64.9	20.1	6.0	9.0
3	3.0	15	3.3	33.4	85.7	36.6	71.7	18.0	4.1	6.2
4	4.0	15	2.8	36.2	88.3	37.8	79.8	14.8	2.0	3.0
5	5.0	15	2.4	41.1	87.2	37.2	90.4	6.1	1.4	2.1
6	7.5	15	1.7	34.6	75.9	32.4	90.3	6.1	1.4	2.2
7	1.0	5.2	2.4	13.0	14.5	17.8	88.9	6.7	1.8	2.6
8	3.0	9.8	2.4	40.0	86.1	36.7	92.9	4.6	1.4	2.1
9	5.0	15	2.4	41.0	87.8	37.5	89.9	7.2	1.1	1.8

[a] Benzene : H_2O_2 = 2 : 1 (mole/mole), the maximum theoretical conversion being 50%.

to benzene was found to be an optimum for achieving a high H_2O_2 utilization and phenol selectivity. At 20 wt% catalyst concentration not only benzene conversion decreases but also phenol selectivity decreases drastically, due to enhanced secondary reactions. It is quite understandable that, due to increased utilization of H_2O_2 for secondary products, the benzene conversion has decreased.

Table 5 illustrates the effect of water concentration on benzene conversion and product selectivities. At a water to benzene ratio = 5 : 1, maintaining 15 wt% catalyst w.r.t. benzene (entries 1–6), maximum benzene conversion as well as optimum H_2O_2 selectivity were observed. Although increasing this ratio beyond 5 with increased dilution resulted in higher phenol selectivity, the benzene conversion and H_2O_2 selectivity decrease considerably. However, decrease of the H_2O : benzene ratio resulted in progressive decrease of benzene conversion, H_2O_2 and phenol selectivities, indicating that at lower dilution secondary reactions (i.e., oxidation of phenol to catechol, hydroquinone, and *p*-benzoquinone) are facilitated. Although, the substrate to catalyst ratio was the same in these experiments, the catalyst concentration with respect to total reaction volume was also changed considerably. Hence, in the next set of experiments, the effect of water to benzene weight ratio was also studied, keeping the catalyst concentration in the total reaction volume constant (at different benzene/catalyst ratios). These results, also given in Table 5 (entries 5, 7–9), suggest that optimum catalyst concentration with respect to both the substrate and the total reaction mixture is needed for achieving high phenol yields (i.e., high H_2O_2 utilization and phenol selectivity).

DISCUSSION

The present results obtained in the hydroxylation of benzene showed that the reaction is very fast under triphase condition compared to that in conventional biphase conditions using an organic co-solvent. Significantly higher activity (as well as high *para* selectivity in the case of substituted benzenes like toluene and anisole (14)) obtained in the triphase system indicates 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 and anisole (14)) probably indicates that under biphase conditions the reaction takes place considerably on the external surface of the catalyst as well. This is further supported by the fact that in triphase the distribution of catechol (CA) and hydroquinone (HQ) was ca 60 : 40 while the same ratio in biphase was ca 40 : 60, indicating higher *para* selectivity in triphase (Table 1).

In relatively hydrophobic 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 in 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 this is true, then it may explain the higher activity in triphase compared to that in biphase. To confirm this hypothesis some competitive adsorption experiments under bi- and tri-phase conditions (in the absence of H_2O_2) were carried out. Figure 5 illustrates the infra red spectra of various TS-1 samples used in the competitive experiments. The TS-1/acetonitrile/benzene sample (sample C, curve C) shows a doublet at ca 2350–2360 cm^{-1} (character-

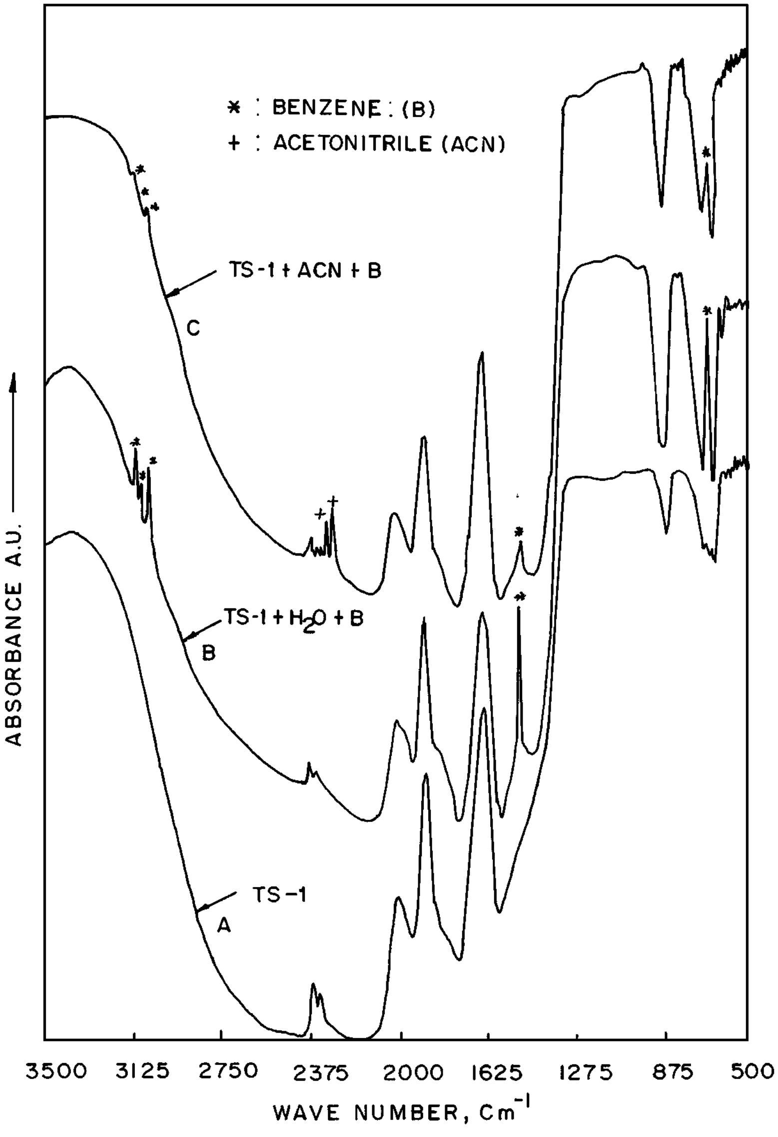

FIG. 5. F.T.-i.r. spectra of different TS-1 samples. A, pure TS-1; B, TS-1/water/benzene; C, TS-1/acetonotrile/ benzene.

istic peaks of acetonitrile (16) in nonoverlapping range with TS-1 vibrations), whereas the TS-1/ H_2O/benzene sample (sample B, curve B) shows major peaks at 3060–3120 cm^{-1} and 1480 cm^{-1}, corresponding to benzene (17). Curve C also indicates the presence of small amount of benzene (peaks represented by asterisk, Fig. 5). It is quite clear from these results that benzene is the main adsorbate in sample B while in sample C acetonitrile is mainly adsorbed. Curve A represents the IR spectrum of the parent TS-1 sample.

Since, the IR measurements were carried out to confirm the relative presence of adsorbate in the TS-1 catalyst, desorption experiments were conducted for quantitative measurement of the adsorbates. The desorbed material from TS-1/acetonitrile/benzene sample (spectrum C, Fig. 5) was mainly acetonitrile (92 wt%), benzene being only 8 wt%. In a similar desorption experiment of TS-1/water/benzene sample (spectrum B, Fig. 5) it was found that ca 90 wt% benzene was desorbed, the remaining being water. The total weight loss was ca 10 wt% on the basis of dry TS-1 in both the cases. These results clearly demonstrate that the presence of acetonitrile provides strong resistance to benzene for diffusion inside the TS-1 channels, while such diffusional hindrance is not encountered by benzene in triphase conditions in the absence of organic solvent, resulting in high conversions in triphase.

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 (intraparticle diffusion) is concerned, the transport of reactant (benzene) to the solid surface through the aqueous phase (external mass transfer) poses an additional problem. Recently, Desikan and Doraiswamy (18) have reviewed this diffusion-reaction problem in triphase catalysis dealing with polymer-supported phase transfer catalysts in various types of triphase catalytic systems, including the solid–liquid–liquid (S-L-L) type. In any such S-L-L systems the overall activity depends on (i) external mass transfer, (ii) intraparticle diffusion, and (iii) 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 most complicated problem in triphase catalysis in general (18).

In our present triphase conditions vigorous stirring, needed for the reaction to occur (external mass transfer, Fig. 3), may help the dispersion of the organic phase in the aqueous one through micro-droplet formation and thereby facilitating the transport of the reactant to the catalyst surface. Although a detailed treatment of chemical engineering and theoretical aspects of this interesting phenomenon is obviously beyond the scope of the present communication, we have tried to interpret the interesting results on the basis of our experimental data.

SUMMARY AND CONCLUSIONS

In summary, it has been demonstrated that using a triphase system (solid–liquid–liquid), in the absence of an organic cosolvent, a considerable increase (ca 20 times) in conversion of benzene during oxidation by the TS-1/H_2O_2 system can be achieved. The effect of various reaction parameters such as time, temperature, benzene to oxidant molar ratio, catalyst concentration, mode of addition of H_2O_2, and dilution level on conversion and selectivity was studied. Vigorous stirring was needed for the reaction to occur in triphase.

Since titanium silicate molecular sieves are relatively hydrophobic in nature, the benzene reactant competes more favorably with water for diffusion and adsorption under triphase conditions, resulting in higher conversion. Apart from enhancement in activity the present triphase method offers distinct advantages in easier product separation and thus contributes to the development of an eco-friendly process.

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REFERENCES

1. Menger, F. M., *J. Am. Chem. Soc.* **92**, 5965 (1970).
2. Starks, C. M., *J. Am. Chem. Soc.* **93**, 195 (1971).
3. Dockx, J., *Synthesis*, 441 (1973).
4. Dehmlow, E. V., *Angew. Chem. Int. Ed. Engl.* **13**, 170 (1974).
5. Regen, S. L., *J. Am. Chem. Soc.* **97**, 5956 (1975).
6. Regen, S. L., *Angew. Chem. Int. Ed. Engl.* **18**, 421 (1979).
7. Molinari, H., Montanari, F., Quici, S., and Tundo, P., *J. Am. Chem. Soc.* **101**, 3920 (1979).
8. Notari, B., *Stud. Surf. Sci. Catal.* **37**, 413 (1987).
9. Thangaraj, A., Kumar, R., Mirajkar, S. P., and Ratnasamy, P., *J. Catal.* **130**, 1 (1991).
10. Thangaraj, A., Kumar, R., and Ratnasamy, P., *J. Catal.* **131**, 294 (1991).
11. Kumar, P., Kumar, R., and Pandey, B., *SYNLETT*, 295 (1995).
12. Kumar, R., Raj, A., Kumar, S. B., and Ratnasamy, P., *Stud. Surf. Sci. Catal. A* **84**, 109 (1994).
13. Thangaraj, A., Kumar, R., and Ratnasamy, P., *Appl. Catal.* **57**, L1-L3 (1990).
14. Bhaumik, A., and Kumar, R., *J. Chem. Soc. Chem. Commun.*, 349 (1995).
15. Kumar, R., Bhaumik, A., Ahedi, R. K., and Ganapathy, S., *Nature* **381**, 298 (1996).
16. The Aldrich Library of Infrared Spectroscopy (C. J. Pouchert, Ed.), ed. III, p. 500. Aldrich, Oklahoma City, 1981.
17. The Aldrich Library of Infrared Spectroscopy (C. J. Pouchert, Ed.), ed. III, p. 560. Aldrich, Oklahoma City, 1981.
18. Desikan, S., and Doraiswamy, L. K., *Indus. Eng. Chem. Res.* **34**, 3524 (1995).