Epoxidation of styrene by anhydrous H_2O_2 over TS-1 and γ-Al_2O_3 catalysts: effect of reaction water, poisoning of acid sites and presence of base in the reaction mixture

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The styrene conversion and product (viz. styrene oxide, phenyl acetaldehyde, benzaldehyde) selectivity in the liquid-phase epoxidation of styrene by H_2O_2 (H_2O_2/styrene = 2) over TS-1 (Si/Ti = 80) and γ-Al_2O_3 are strongly influenced by the presence of water and/or base (*viz.* urea and pyridine) in the reaction mixture. The TS-1 showed high styrene conversion activity but no epoxide selectivity in the absence of any base. When anhydrous H_2O_2 (24% H_2O_2 in ethyl acetate), with the continuous removal of the reaction water (using the Dean–Stark trap), was used instead of 50% aqueous H_2O_2, both the conversion and epoxide yield are increased drastically for the γ-Al_2O_3, whereas for the TS-1, the increase in the conversion was quite small and there was also no improvement in the epoxide selectivity and/or yield. However, when urea or pyridine was added in the reaction mixture, the epoxide selectivity for both the catalysts was increased depending on the concentration of the base added; the increase in the selectivity was very large for the TS-1 but small for the γ-Al_2O_3. Poisoning of the acid sites of the γ-Al_2O_3 by the chemisorbed ammonia or pyridine (at 100 °C) caused a small decrease in the conversion, but it also caused a large decrease in the epoxide selectivity. However, the pyridine poisoning of the TS-1 caused a little beneficial effect, a small increase in the epoxide selectivity. The ammonia poisoning of the TS-1, however, resulted in a small decrease in the conversion with no improvement in the epoxide selectivity. As compared to the TS-1, the γ-Al_2O_3 catalyst showed a much better performance in the epoxidation by anhydrous H_2O_2 with the continuous removal of the reaction water. However, the reaction water, if not removed continuously, is detrimental to the γ-Al_2O_3, causing a large decrease in the catalytic activity and selectivity for styrene oxide but an increase in the selectivity for benzaldehyde.

KEY WORDS: epoxidation of styrene; anhydrous hydrogen peroxide; TS-1 catalyst; γ-Al_2O_3 catalyst; catalyst poisoning of acid sites.

1. Introduction

Catalytic liquid-phase epoxidation of styrene is a practically important reaction for the production of styrene oxide, which is an important organic intermediate. A few studies have been reported earlier on the epoxidation of styrene over Ti/SiO_2 [1–3], TS-1 [3–6], Ti-MCM-41 [6], Fe or V/SiO_2 [3] and TBS-2 and TS-2 [7] catalysts using TBHP [1], aqueous H_2O_2 [2–4,6,7] or urea-H_2O_2 adduct [5], as an oxidizing agent. High styrene oxide selectivity (>80%) was observed when TBHP [1] and urea–H_2O_2 adduct [5] were used as the oxidizing agent but only at a low styrene conversion (9.8 and 17.7% respectively). When an aqueous H_2O_2 was used as the oxidizing agent, the styrene oxide selectivity for all the above catalysts was very poor. It is, therefore, of practical interest to achieve high styrene oxide selectivity, particularly at a high styrene conversion.

The present work was undertaken with the following two objectives: (1) To improve both the activity and selectivity of TS-1 in the epoxidation of styrene by using anhydrous H_2O_2 as (H_2O_2 in ethyl acetate) an oxidizing agent by continuously removing the water formed in the reaction, and also by poisoning the acid sites of the catalyst by a base (*viz.* pyridine or ammonia) or by adding a base (pyridine or urea) in the reaction mixture, and (2) to compare the performance of TS-1 with that of γ-alumina (which is a much cheaper catalyst) for the epoxidation and also for H_2O_2 (anhydrous) decomposition, under identical conditions.

2. Experimental

TS-1 (Si/Ti = 80) was prepared by a procedure similar to that described earlier [5]. Its MFI structure was confirmed by XRD. It was further characterized by scanning electron microscopy for its crystal size (0.2–0.3 μm), by diffuse reflectance UV–Vis spectroscopy and FTIR for the incorporation of its Ti in the zeolite framework, by nitrogen adsorption at liquid nitrogen temperature for its surface area (410 $m^2\,g^{-1}$) and also by chemisorption of ammonia (at 100 °C) for its acidity (0.26 $mmol\,g^{-1}$).

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γ-Alumina was obtained by calcining boehmite in a muffle furnace at 600 °C for 2 h. It was also characterized by the XRD, nitrogen adsorption and ammonia chemisorption. Its surface area and acidity was found to be $205\,m^2\,g^{-1}$ and $0.053\,mmol\,g^{-1}$ respectively.

Catalytic epoxidation of styrene over the TS-1 and γ-alumina catalysts was carried out in a magnetically stirred glass reactor (capacity: $25\,cm^3$) under reflux (bath temperature = 107 °C), using aqueous H_2O_2 (50% H_2O_2 in water) or non-aqueous (anhydrous) H_2O_2 (24% H_2O_2 in ethyl acetate) as an oxidizing agent and ethyl acetate as a solvent with or without the continuous removal of the water formed in the reaction. The continuous removal of the reaction water (when anhydrous H_2O_2 was used as the oxidizing agent) was accomplished by using the Dean–Stark trap between the reactor and the reflux condenser. The vapors of reaction mixture (mostly ethyl acetate and water formed in the reaction) are condensed in the reflux condenser and the condensate is continuously collected in the Dean–Stark trap, forming a water layer at the bottom and an ethyl acetate layer at the top. The ethyl acetate is continuously fed back to the reaction flask and the reaction water is removed from the bottom of the trap using a stopcock, while maintaining the initial level of water in the trap. The anhydrous H_2O_2 (24% H_2O_2 in ethyl acetate) was obtained by refluxing an aqueous H_2O_2 (50% H_2O_2 in water) with ethyl acetate, and thereby removing the water from the aqueous H_2O_2, using the Dean–Stark trap. The amount of H_2O_2 present in the anhydrous H_2O_2-ethyl acetate or in the reaction mixture after the epoxidation reaction was determined by decomposing the H_2O_2 by MnO_2 and measuring the amount of oxygen produced in the H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5O_2$) quantitatively, using a constant pressure gas collector [8]. The unconverted styrene and reaction products (*viz.* styrene oxide, phenyl acetaldehyde and benzaldehyde) were analyzed by gas chromatography, using an SE-30 (on chromosorb-W) column and a flame ionization detector. The conversion, product selectivity and product yield were calculated as follows: conversion (%) = [(moles of reactant converted) × 100] ÷ [moles of reactant in feed], product selectivity (%) = [(moles of product formed) × 100] ÷ [moles of reactant converted] and product yield (%) = (percentage of reactant converted to a particular product) or [conversion (%) × product selectivity (%) ÷ 100].

Poisoning of acid sites of both the catalysts by ammonia or pyridine was carried out by saturating the catalyst (preheated in a flow of moisture-free nitrogen at 400 °C for 1 h) with the base at 100 °C and then flushing the saturated catalyst by moisture-free nitrogen (space velocity = $3000\,cm^3\,g^{-1}\,h^{-1}$) at the same temperature for a period of 1 h.

3. Results and discussion

The incorporation of most of the Ti in the framework of the TS-1 sample was confirmed by observing the absorption band at 210 nm and the absence of any absorption band at about 325 nm in the UV–Vis spectra of the TS-1 [6,9,10], as shown in figure 1, and also by observing the IR band $960\,cm^{-1}$, which is used as the fingerprint of the Ti incorporation in the framework of silicalite [7,10,11]. The acidity of the TS-1 and γ-alumina catalysts was measured in terms of the ammonia chemisorbed at 100 °C; it was found to be 0.26 and $0.053\,mmol\,g^{-1}$ respectively.

These two catalysts are compared in figure 2 for their H_2O_2 decomposition activity with or without the continuous removal of the reaction water, and also in table 1 for their performance in the epoxidation of styrene by aqueous H_2O_2 or anhydrous H_2O_2 (with the continuous removal of the water formed in the reaction) in the presence or absence of urea in the reaction mixture. The results (table 1) show a strong influence of the presence of urea on the product selectivity for both the catalysts; the influence is very drastic for TS-1. The presence of water (i.e., the use of aqueous H_2O_2) has a large effect on the styrene conversion activity of the alumina, but the effect for the TS-1 is very small. For both the catalysts, the H_2O_2 decomposition rate is, however, increased because of the continuous removal of the reaction water (figure 2).

Results showing the variation of styrene conversion and product selectivity with the reaction period in the epoxidation by anhydrous H_2O_2 over the alumina catalyst, with or without the continuous removal of the reaction water, are presented in figure 3. Both the styrene conversion and the styrene oxide selectivity are appreciably increased because of the continuous removal of the reaction water. It is also interesting to note that, when the reaction water is removed continuously, the selectivity for styrene oxide is increased and that for phenyl acetaldehyde is decreased by increasing the reaction time. But, when the reaction water is not removed, the selectivity for styrene oxide is increased initially and then decreased by increasing the reaction time; the benzaldehyde selectivity has exactly the opposite trend.

Results in table 2 show the effect of poisoning by the ammonia or pyridine chemisorption (at 100 °C) of the acid sites present in the two catalysts on their performance in the epoxidation. The poisoning of acid sites of the TS-1 by ammonia has little or no effect on its styrene conversion activity or product selectivity, but the poisoning by pyridine resulted in an appreciable decrease in its activity and also in a small increase in its styrene oxide selectivity, whereas, for the alumina catalyst, the poisoning by ammonia or pyridine caused a small decrease in the activity but an appreciable decrease in the styrene oxide selectivity.

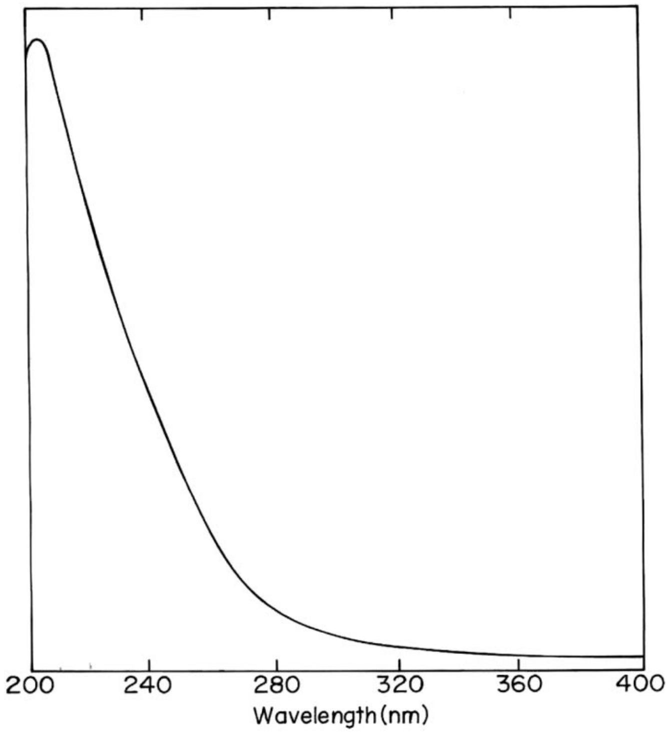

Figure 1. UV–Vis spectra of TS-1 catalyst.

The effect of pyridine added to the reaction mixture on the performance of the TS-1 and γ-alumina catalysts in the epoxidation of styrene by anhydrous H_2O_2 (with the continuous removal of the reaction water) is shown in figures 4 and 5. In both the cases, the styrene conversion is decreased and the selectivity of styrene oxide is increased but that for phenyl acetaldehyde is decreased by increasing the pyridine concentration.

3.1. Decomposition of anhydrous H_2O_2

For both the catalysts, the rate of H_2O_2 decomposition was higher when the water formed in the decomposition was removed continuously during the reaction (figure 2). The H_2O_2 decomposition activity of both the catalysts is more or less similar when the water of reaction was removed continuously. However, the H_2O_2 decomposition, without the removal of water was faster for the alumina catalyst. This is consistent with the fact that the acidity of the alumina catalyst (0.053 mmol g^{-1}) is much lower than that (0.26 mmol g^{-1}) of the TS-1 catalyst. In the presence of the reaction water, the Lewis acid sites of TS-1 are expected to be converted into protonic ones. Since H_2O_2 is stabilized in the presence of protonic acid sites, its decomposition rate is decreased when the reaction water is not removed continuously from the reaction mixture, whereas in the case of alumina, the reaction water is expected to destroy its Lewis acidity and deactivate the catalyst gradually because of its hydrophilic nature.

3.2. Epoxidation of styrene by aqueous H_2O_2

In the absence of urea, the TS-1 showed high styrene conversion activity (71.7%) but no selectivity or yield for styrene oxide. However, its epoxide selectivity was

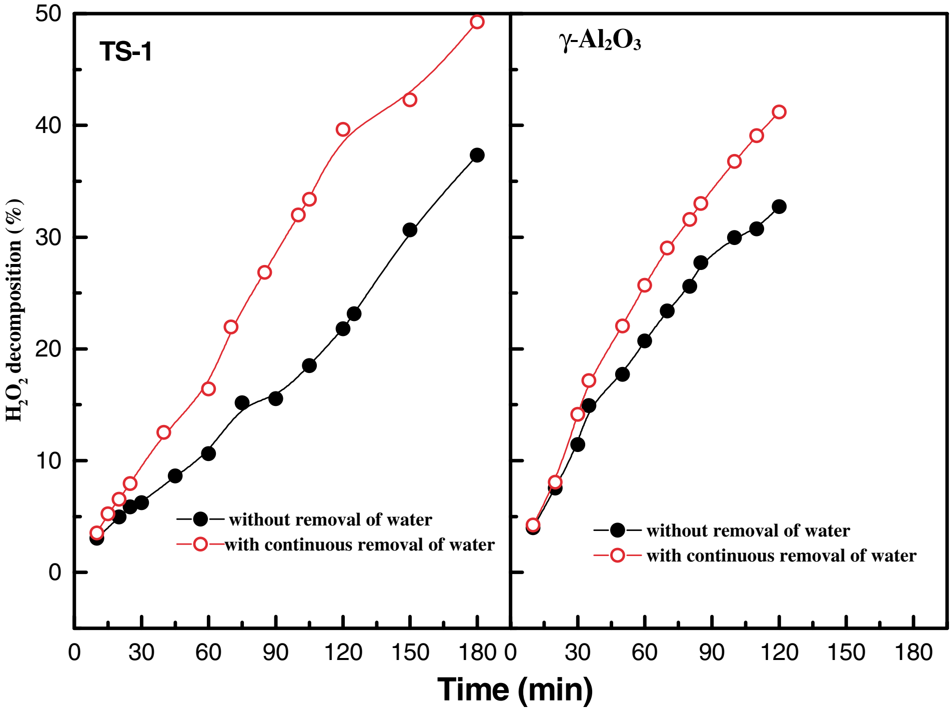

Figure 2. Decomposition of anhydrous H_2O_2 over TS-1 and γ-Al_2O_3 catalysts with or without the removal of the water of the reaction (reaction mixture = 40 mmol anhydrous H_2O_2 + 9 mL ethyl acetate + 0.4 g catalyst, temperature under reflux).

Table 1

Epoxidation of styrene by aqueous H_2O_2 (50% H_2O_2 in water) and anhydrous H_2O_2 (24% in ethyl acetate) over TS-1 and γ-Al_2O_3 catalysts [reaction mixture = 20 mmol styrene + 40 mmol H_2O_2 (aqueous or anhydrous) + 0.4 g catalyst + 9 mL ethyl acetate + urea (urea/H_2O_2 mole ratio = 0–1.0) and reaction period = 5 h]

Oxidizing agent	Urea/H_2O_2 ratio	Continuous removal of the water formed (yes or no)	Conversion (%)		Selectivity (%)[b]			Styrene conversion rate (mmol g^{-1} h^{-1})
			Styrene	H_2O_2	SO	PA	B	
Catalyst TS-1								
Aqueous H_2O_2	0.0	No	71.7	100	0.0	60.3	39.7	7.2
Aqueous H_2O_2	1.0	No	28.8	100	77.1	13.8	9.1	2.9
Anhydrous H_2O_2	0.0	Yes[a]	72.9	100	0.0	57.3	43.7	7.3
Anhydrous H_2O_2	0.04	Yes[a]	21.9	97.8	62.8	13.6	23.6	2.2
Catalyst γ-Al_2O_3								
Aqueous H_2O_2	0.0	No	8.3	53.9	7.9	9.7	82.3	0.8
Aqueous H_2O_2	0.1	No	6.4	42.5	50.8	11.6	37.6	0.6
Anhydrous H_2O_2	0.0	Yes[a]	47.9	100	53.5	20.6	25.9	4.8
Anhydrous H_2O_2	0.04	Yes[a]	21.4	93.1	67.8	11.9	20.3	2.1

[a] The reaction water was removed continuously using Dean–Stark trap.

[b] SO = styrene oxide, PA = phenyl acetaldehyde, B = benzaldehyde.

increased drastically (from 0 to 77.2%) while the conversion was decreased appreciably (from 77.1 to 28.8%), and its selectivity for benzaldehyde and phenyl acetaldehyde also was decreased markedly because of the addition of urea in the reaction mixture (table 1). Increase in the epoxide selectivity due to urea addition is consistent with that observed earlier [5].

It is interesting to note that, in the absence of urea, the alumina showed much higher selectivity for benzaldehyde, whereas the TS-1 showed higher selectivity for phenyl acetaldehyde.

Under identical conditions, the alumina catalyst showed much less styrene conversion activity, but it showed some epoxide selectivity. After urea addition, its styrene conversion activity and benzaldehyde selectivity were decreased, but its selectivity for styrene oxide and phenyl acetaldehyde was increased. The increase in the epoxide selectivity was quite large and this is consistent with that observed for the TS-1.

3.3. *Epoxidation of styrene by anhydrous* H_2O_2

When the anhydrous H_2O_2 (with the continuous removal of the reaction water) instead of the aqueous H_2O_2 was used in the epoxidation, there was a small change in the performance of the TS-1 (table 1). However, because of the use of anhydrous H_2O_2, the performance of the alumina catalyst was changed drastically; its styrene conversion activity and also its selectivity for styrene oxide and phenyl acetaldehyde were increased; the increase in the activity and epoxide selectivity was very large.

It may be noted that, in the present studies, the alumina catalyst showed good styrene oxide selectivity (53.5%) even at high styrene conversion (47.9%). In the earlier studies, high styrene oxide selectivity was reported, but at much lower conversion of styrene [1,5]. The high conversions reported in the earlier work on the epoxidation of styrene over TS-1 [4,5] were extrapolated for the styrene/H_2O_2 mole ratio of 1.0 from the styrene/H_2O_2 ratio of 4.0, assuming that the selectivity is independent of the reactant ratio and/or the styrene conversion, which is generally not true.

3.3.1. *Effect of the reaction water*

A comparison of the results in figure 3 show a strong influence of the reaction water on the epoxidation over the alumina catalyst. Because of the continuous removal of the reaction water,

- the styrene conversion is increased markedly,
- the styrene oxide selectivity is increased, particularly at the higher reaction periods, and
- the benzaldehyde selectivity is decreased.

When the reaction water was not removed continuously, its accumulation at the higher reaction periods led to the lowering of both the conversion and styrene oxide selectivity. Catalyst deactivation is expected because of adsorption and absorption of the reaction water, causing surface hydrolysis of the alumina. The observed higher benzaldehyde selectivity in this case is consistent with that observed when the aqueous H_2O_2 was used in the epoxidation (table 1). The accumulated reaction water was also found to cause the formation of catalyst lumps (containing the water), which adhered to the reactor walls, drastically reducing the suspension of the catalyst particles in the reaction mixture. This is expected because of the hydrophilic nature of the catalyst.

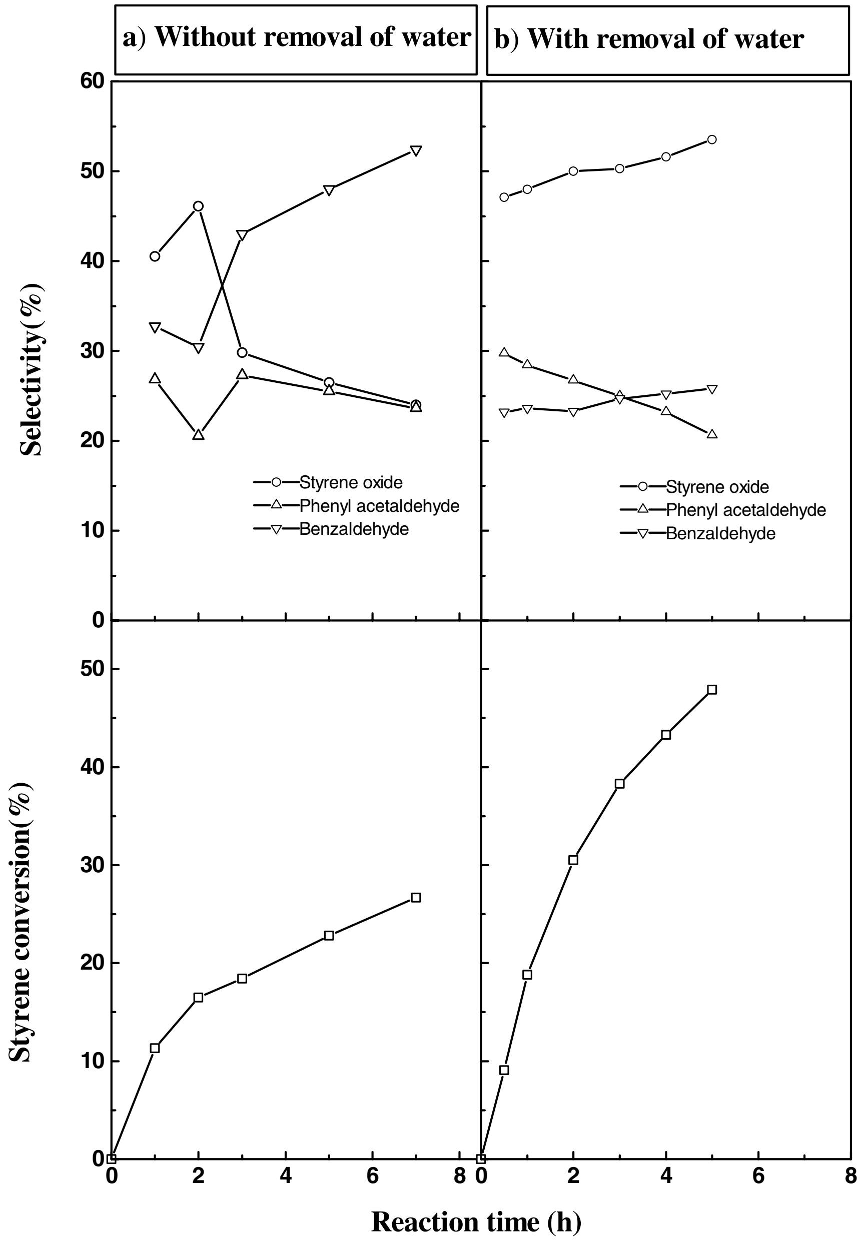

Figure 3. Variation with reaction period of styrene conversion and product selectivity in the epoxidation by anhydrous H_2O_2 over the γ-Al_2O_3 with or without the continuous removal of the reaction water (reaction mixture = 20 mmol styrene + 40 mmol anhydrous H_2O_2 + 9 mL ethyl acetate + 0.4 g catalyst).

Table 2
Effect of poisoning the TS-1 and γ-Al_2O_3 catalysts (by chemisorption of ammonia or pyridine at 100Stark trap (reaction mixture = 20 mmol styrene + 40 mmol anhydrous H_2O_2 + 9 mL ethyl acetate + 0.4 g catalyst and reaction period = 5 h)

Catalyst	Poisoning agent	Conversion (%)		Selectivity (%)[a]			Styrene conversion rate
		Styrene	H_2O_2	SO	PA	B	(mmol g^{-1} h^{-1})
TS-1	Without poisoning	72.9	100	0.0	57.3	42.7	7.3
TS-1	Ammonia	68.8	78.4	0.0	56.3	43.7	6.9
TS-1	Pyridine	44.2	81.2	5.2	61.7	33.1	4.4
γ-Al_2O_3	Without poisoning	47.9	100	53.5	20.6	25.8	4.8
γ-Al_2O_3	Ammonia	46.1	95.4	28.1	30.2	41.7	4.6
γ-Al_2O_3	Pyridine	47.1	100	41.2	20.9	37.9	4.7

[a] SO = styrene oxide, PA = phenyl acetaldehyde, B = benzaldehyde.

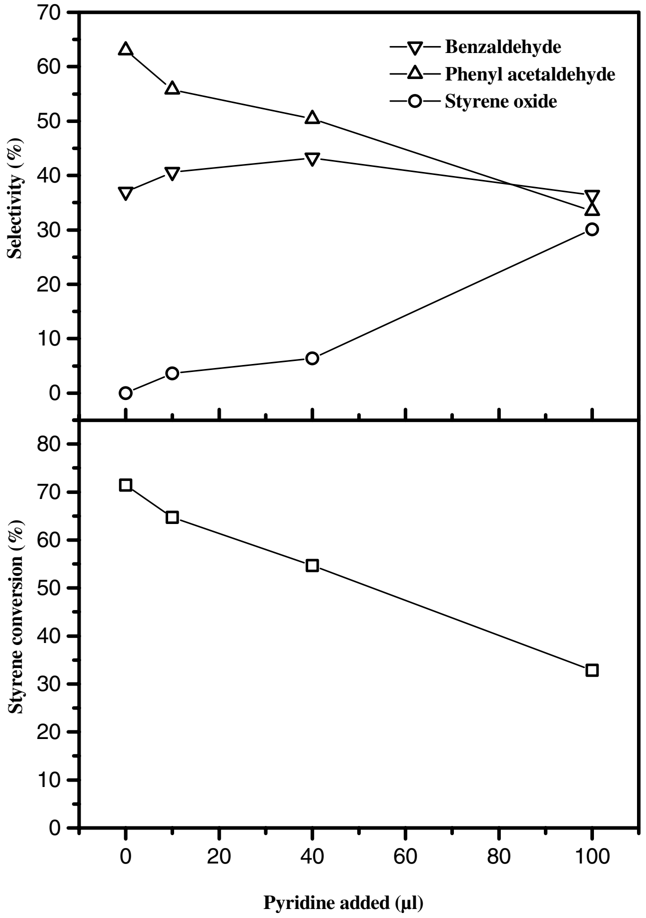

Figure 4. Effect of pyridine added to the reaction mixture on the styrene conversion and product selectivity in the epoxidation of styrene by anhydrous H_2O_2 with the continuous removal of the water of the reaction over TS-1 zeolite (reaction mixture = 20 mmol styrene + 40 mmol anhydrous H_2O_2 + 9 mL ethyl acetate + 1.0 g catalyst + pyridine (0–100 μL) and reaction period = 2 h).

The above observations clearly showed that the reaction water, if not removed continuously, is detrimental to the alumina catalyst in the epoxidation. Catalyst deactivation by the reaction water was also observed earlier for the epoxidation of cyclohexene and 1-octene by anhydrous H_2O_2 (without the removal of the reaction water) over alumina [12]. However, the presence of water even in much larger amounts has only a small effect on the performance of the TS-1 (table 1).

3.3.2. *Effect of the reaction period (or conversion) on product selectivity*

In the epoxidation over the alumina catalyst with the continuous removal of the reaction water (figure3(b)), the selectivity for styrene oxide is increased and that for phenyl acetaldehyde is decreased by increasing the reaction time (or consequently increasing the styrene conversion). When the reaction water is not removed continuously, in the initial short reaction period, as expected there is only a small effect of the reaction water on the product selectivity (figure 3(a)). But, after the initial period, the continuously increasing accumulated reaction water caused the observed decrease in the styrene oxide selectivity with increasing reaction time.

3.3.3. *Effect of the poisoning of acid sites*

The results in table 2 indicate that the poisoning of acid sites by the chemisorbed ammonia (at 100 °C) resulted in a small decrease in the styrene conversion activity of both the catalysts. The poisoning by ammonia caused little or no change in the product selectivity for the TS-1 but a substantial decrease in the epoxide selectivity for the Al_2O_3 catalyst.

The effect of the poisoning by pyridine on the epoxidation over the alumina catalyst was more or less similar to that of the poisoning by ammonia. However, for the TS-1, its poisoning by pyridine resulted in a large decrease in its styrene conversion activity and also in a small increase in its epoxide selectivity (from 0 to 5%). On the contrary, its poisoning by ammonia had little or no effect on its performance in the epoxidation. It is believed that the low epoxide selectivity of TS-1 is attributed to the isomerization of styrene oxide, once formed, to phenyl acetaldehyde. However, the results of poisoning, by ammonia or pyridine indicate that it is not so. This is also supported by the results showing the strong influence of the presence of pyridine in the reaction mixture at different concentrations on the epoxidation over the TS-1 catalyst (figure 4). The addition of 10 μL of pyridine resulted in an increase in the epoxide selectivity from 0 to 3.6% with a decrease in the styrene conversion from 71.2 to 65.7%. Thus, even at the pyridine concentration, which is high enough to block most of the acid sites on the TS-1, there was only a small increase in the epoxide selectivity.

3.3.4. *Effect of urea in the reaction mixture*

The results in table 1 indicate that, in the absence of urea, the TS-1 catalyst shows high styrene conversion activity but no selectivity for styrene oxide. However, its activity is decreased but shows good selectivity for the epoxide, when urea (urea/H_2O_2 = 0.04) is added to the anhydrous reaction mixture. In the case of the alumina catalyst also, a decrease in the activity but an increase in the epoxide selectivity due to the presence of urea in the reaction mixture is observed (table 1). The decrease in the styrene conversion activity of both the catalysts due to the presence of urea is expected mostly because of the blockage of catalytic active sites by adsorbed urea on the catalyst and/or due to the formation of H_2O_2-urea adduct, which is less reactive than H_2O_2. However, the increase in the epoxide selectivity due to the presence of urea may be because of the protection of epoxide, once formed, by the urea itself (which is basic in nature). Since the TS-1 catalyst showed no epoxide selectivity even when the H_2O_2 used was anhydrous (table 1), the earlier explanation based on the dehydrating ability of

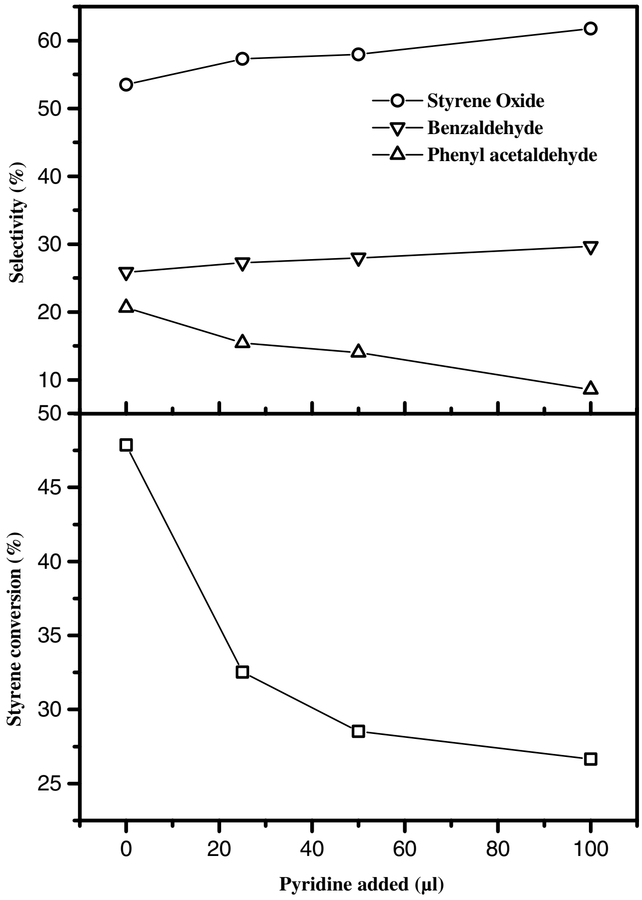

Figure 5. Effect of pyridine added to the reaction mixture on the styrene conversion and product selectivity in the epoxidation of styrene by anhydrous H_2O_2 with the continuous removal of the water of the reaction over γ-Al_2O_3 (reaction mixture = 20 mmol styrene + 40 mmol anhydrous H_2O_2 + 9 mL ethyl acetate + 0.4 g catalyst + pyridine (0–100 μL) and reaction period = 5 h).

urea to make available an anhydrous H_2O_2 for the epoxidation reaction for the increase in the epoxide selectivity [5] is not valid.

3.3.5. Effect of pyridine in the reaction mixture

The results in figures 4 and 5 clearly show a strong influence of the presence of pyridine in the reaction mixture on the performance of both the catalysts. For both the catalysts, their styrene conversion activity is decreased markedly and their selectivity for the epoxide is increased but that for phenyl acetaldehyde is decreased with increasing pyridine concentration; the increase in the epoxide selectivity for TS-1 is much higher and also exponential. However, the effect of the presence of pyridine on the benzaldehyde selectivity for both the catalysts is found to be small. The results of the poisoning by pyridine for both the catalysts (table 2) clearly show that the observed increase in the epoxide selectivity due to the presence of pyridine in the reaction mixture cannot just be due to the blockage of acid sites on the catalyst by the chemisorbed pyridine. Increase in the selectivity is probably attributed to the stabilization of styrene oxide by its interaction with the pyridine present in the bulk solution, similar to that observed earlier [13]. The decrease in the styrene conversion with increasing pyridine concentration is, however, expected probably because of the formation of H_2O_2-pyridine adduct (because of the acidic nature of H_2O_2) and/or the reversible adsorption of pyridine on both the catalysts, occupying more and more catalytically active sites.

The results (table 1 and figures 4 and 5) also indicate that, as compared to TS-1, γ-Al_2O_3 is a better catalyst for the epoxidation by anhydrous H_2O_2. Alumina also showed high epoxide selectivity and yield in earlier studies on the epoxidation of cyclooctene, cyclohexene, limonene, and 1-octene by anhydrous H_2O_2 without the removal of the reaction water [12]. The styrene epoxidation by anhydrous H_2O_2 over the alumina catalyst seems to involve Al-O-OH species ($>$Al-OH + $H_2O_2 \rightarrow >$Al-O-OH + H_2O), similar to that described by Mandelli *et al.* [12]. The formation of Al-O-OH species is expected to be suppressed in the presence of water but enhanced by the removal of the reaction water using the Dean–Stark trap and/or using urea because of its dehydrating ability. This is quite consistent with what was observed.

4. Conclusions

Performance of the TS-1 and γ-Al_2O_3 catalysts, with or without poisoning of their acid sites (by ammonia or pyridine), has been evaluated for the epoxidation of styrene by aqueous or anhydrous H_2O_2 (with or without the continuous removal of the reaction water) in the presence or absence of urea or pyridine. From these studies, the following important conclusions have been drawn:

(1) In both the presence and absence of water, the TS-1 shows high styrene conversion activity but no selectivity for styrene oxide, whereas, in the absence of water, the γ-alumina is both an active and a selective catalyst for the epoxidation of styrene to styrene oxide. In the absence of water, the styrene conversion activity of both the catalysts is increased; the increase is very small for TS-1 but it is drastic for γ-Al_2O_3. Even the accumulation of the reaction water has a large adverse effect on the performance of γ-Al_2O_3. The effect of water on the performance of TS-1 is, however, very small.

(2) The TS-1 becomes selective for the styrene-to-styrene oxide conversion after the addition of a base (*viz.* urea or pyridine) in the reaction mixture, depending upon the base concentration. The styrene oxide selectivity for γ-Al_2O_3 is also increased in the presence of urea or pyridine in the reaction mixture; it is increased with increasing pyridine concentration.

(3) Poisoning of the acid sites by the chemisorbed ammonia or pyridine (at 100 °C) causes an appreciable decrease in its styrene conversion activity but only a little improvement in the epoxide selectivity (for the poisoning by pyridine) or none at all (for the poisoning by ammonia) for the TS-1, whereas the poisoning results in an appreciable decrease in both the selectivity and the yield of styrene oxide for the γ-Al_2O_3.

(4) When the reaction water is removed continuously, both the TS-1 and the γ-Al_2O_3 catalysts have more or less the same H_2O_2 decomposition activity. However, the γ-Al_2O_3 is a better catalyst for the epoxidation by anhydrous H_2O_2 with the continuous removal of the reaction water.

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