Epoxidation of styrene with TBHP/O_2 over ferrierite (FER) type molecular sieves

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Epoxidation of styrene over vanadium silicalite with ferrierite (FER) type topology is undertaken. Influence of temperature, pressure, various solvents and solvent to substrate mole ratio was investigated. Conversion increased with increase in temperature and pressure. Solvent to substrate mole ratio is found to play a crucial role in increasing the conversion and selectivity. Catalytic activity of V-FER was compared with those of Ti-FER, TS-1 and Fe-FER. In the case of V- and Ti-ferrierite analogs, styrene oxide was the major product, whereas phenylacetaldehyde was the major product in the case of TS-1. The catalyst could be recycled after washing by a suitable solvent such as acetone and showed no significant loss in catalytic activity.

Keywords: V-FER, Ti-FER, epoxidation, styrene oxide, TBHP

1. Introduction

The epoxidation of alkenes constitutes one of the most useful reactions in organic synthesis, as the epoxide group is an active intermediate, which can be readily transformed to the required functionality in a stereospecific manner. Styrene oxide (obtained by epoxidation of styrene) is a commercially important material used for UV-absorbers, drugs, perfumes, sweeteners, etc. Moreover, it can also be used as one of the epoxy resin reactive diluents as chain terminating elements to reduce cross-linking density. A number of reports [1–4] for the preparation of styrene oxide using various metal complexes and encapsulated zeolite as catalysts in a homogeneous medium are cited in the literature. However, the selectivity towards styrene oxide is lower (5–35%) and the major product is benzaldehyde. The oxidation of styrene by H_2O_2 on several molecular sieves treated with $TiCl_4$ vapors is also reported [5], in which case the conversion of styrene is 12% and the total selectivity of styrene epoxide and phenylacetaldehyde is 55.9%. Neri et al. [6] and Kumar et al. [7] performed a similar reaction over a TS-1 catalyst, wherein phenylacetaldehyde is the major product. Styrene epoxidation by air [9] is also patented. However, in these processes the selectivity of styrene oxide was low (18–35%).

Ferrierite has been found to be an excellent acidic catalyst especially for skeletal isomerization [10,11]. Recently, V, Ti and Fe were substituted isomorphously in the FER topology. Since high conversion of styrene was reported on TS-1 catalyst, a metallosilicate ferrierite being a metallosilicate with different structure, we explore the oxidative properties of Ti-, Fe- and V-ferrierite in the epoxidation of styrene using molecular oxygen as the oxidant and TBHP as the initiator. Styrene oxidation over the Ti-/V-FER towards styrene epoxide shows higher selectivity than that of homogeneous complexes and encapsulated zeolites.

2. Experimental

2.1. Synthesis

The catalysts V-FER [12], TS-FER [13] and Fe-FER [14] were synthesized according to the methods described in the literature. The molar compositions of the catalysts used in the reaction are given in table 1. The catalysts were calcined to remove the occluded organic template. Extra-framework vanadium, in the case of V-FER, was removed by ammonium acetate treatment. The Fe-FER catalyst was converted to its H-form by repeated ion exchange treatment with 0.2 M ammonium nitrate solution at 80 °C followed by calcination at 480 °C.

2.2. Characterization

The phase purities of T-, V- and Fe-FER obtained were determined by X-ray powder diffraction (Rigaku, D-Max III VC diffractometer with Cu $K\alpha$ radiation of $\lambda = 1.5404$ Å). The chemical compositions of silica, titanium, vanadium and iron for respective FER catalysts were established by a wavelength dispersive XRF (3070 Rigaku) spectrophotometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in flowing air ($3\ \mathrm{dm^3\,h^{-1}}$) at a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ on an autonomic TG/DTA (SETRAM 92). The crystal size and morphology was examined by a scanning electron microscope 440 stereoscan (Cambridge, UK). Fe-, Ti- and V-FER

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Table 1
Chemical compositions of the catalysts under study.

Catalyst	Input composition[a]	Output ratio (by XRF)	Si/M ratio after reaction (by XRF)
V-FER (HR)	$10.78\text{Py} : 5.45\text{PA} : \text{SiO}_2 : 0.01\text{V}_2\text{O}_5 : 1.4\text{HF/Py} : 2.76\text{H}_2\text{O}$	Si/V = 120	Si/V = 122
V-FER (LR)	$10.78\text{Py} : 5.45\text{PA} : \text{SiO}_2 : 0.025\text{V}_2\text{O}_5 : 1.4\text{HF/Py} : 2.76\text{H}_2\text{O}$	Si/V = 18	Si/V = 19
TS-FER	$10.78\text{Py} : 5.45\text{PA} : \text{SiO}_2 : \text{TiO}_2 : 1.4\text{HF/Py} : 2.76\text{H}_2\text{O}$	Si/Ti = 114	Si/Ti = 115
TS-1	Synthesized according to [7]		
Fe-FER	$\text{Na}_2\text{O} : \text{Pyrr} : \text{SiO}_2 : \text{Fe}_2\text{O}_3{\cdot}\text{H}_2\text{O}$	Si/Fe = 16	Si/Fe = 17
V-impregnated	$\text{SiO}_2 : 0.025\text{V}_2\text{O}_5$		

[a] Py = pyridine, PA = propylamine and Pyrr = pyrrolidine.

were further characterized by UV-visible spectroscopy (Shimadzu UV2101PC) and FTIR (Nicolet FTIR).

2.3. Catalytic activity

The catalyst used for the present study was activated in a flow of air at 573 K for 3–5 h. A typical reaction procedure includes addition of acetone (6.96 g, 0.12 mol) to styrene (0.502 g, 5 mmol) followed by addition of TBHP (0.05 g, 70% s.d. Fine Chemicals Ltd.). Finally, activated V-FER catalyst (0.05 g) was added to the solution. The total mass was then transferred into a closed high-pressured stirred autoclave (Parr 4842, USA). The autoclave was pressurized to 200 psi by air and the mass was heated from ambient to the desired temperature (time taken to reach the desired temperature was approximately 15–20 min) and maintained for 30 min. Finally, the autoclave was quenched with cold water. Same procedure was followed for all the other runs.

2.4. Product analysis

The product was filtered and analyzed by GC (Shimadzu GC-15 A, packed column SE-30 and FID as detector). The product was confirmed by GCMS (Shimadzu GCMS-QP 2000A, SC-52 column) and GCFTIR (Perkin–Elmer, FTIR spectrometer spectrum 2000).

3. Results and discussion

The catalysts used for the reaction were highly crystalline without any impurity phase and had the output ratios as indicated in table 1. After the reaction, in the case of V-FER, there was no indication of vanadium leaching from the catalyst, as confirmed by XRF analysis (table 1). The primary products of the reaction were styrene oxide and benzaldehyde. Under our reaction conditions it is believed that part of styrene oxide formed was isomerized to phenylacetaldehyde and the formation of benzoic acid was due to the successive oxidation of benzaldehyde. The higher regioselectivity towards phenylacetaldehyde than acetophenone during the isomerization of styrene oxide may be due to the formation of more stable α cation adjacent to the phenyl ring [16].

3.1. Effect of solvent to styrene ratio

Figure 1 highlights the influence of the acetone to styrene molar ratio on the conversion and the selectivity for styrene epoxide. Solvent dilution was found to have a profound effect on the reaction. When the acetone to styrene molar ratio was increased to 25, the conversion increased significantly along with an increase in selectivity for styrene epoxide with a decrease in formation of benzaldehyde. However, further increase in acetone to styrene molar ratio did not exhibit any significant change both in styrene conversion and selectivity for styrene oxide. Dilution reduces the polymerization of styrene monomer thus favoring the epoxidation.

3.2. Effect of solvent polarity

Table 2 summarizes the effect of solvent polarity on the styrene epoxidation reaction. It was observed that with the increase in solvent polarity the conversion and selectivity for epoxide increased. A non-polar solvent such as cyclohexane showed lower conversion and selectivity as compared to a polar solvent such as acetone. Furthermore, it is known [7] that an aprotic solvent such as acetone, acetonitrile, etc. favors this reaction.

3.3. Effect of temperature and pressure on styrene epoxidation

Table 3 describes the effect of temperature as well as pressure on styrene epoxidation. As expected, the conversion increased with the increase in temperature, however, the increase in selectivity for styrene epoxide was not linear. When the temperature was increased from 353 to 373 K (at 200 psi), selectivity for styrene oxide increased, but on further increase of temperature (i.e., to 393 K) the selectivity for benzaldehyde and phenylacetaldehyde increased at the expense of styrene oxide. According to Reddy et al. [16] at lower temperature cleavage of the olefinic bond (C=C) was higher while at higher temperature formation of epoxide seems to be favored.

Figure 2 displays the influence of pressure at 373 K. The conversion increased with the increase in pressure. When the pressure was increased from 100 to 300 psi the selectivity for styrene oxide remained nearly constant, however, selectivity for phenylacetaldehyde as well as others increased

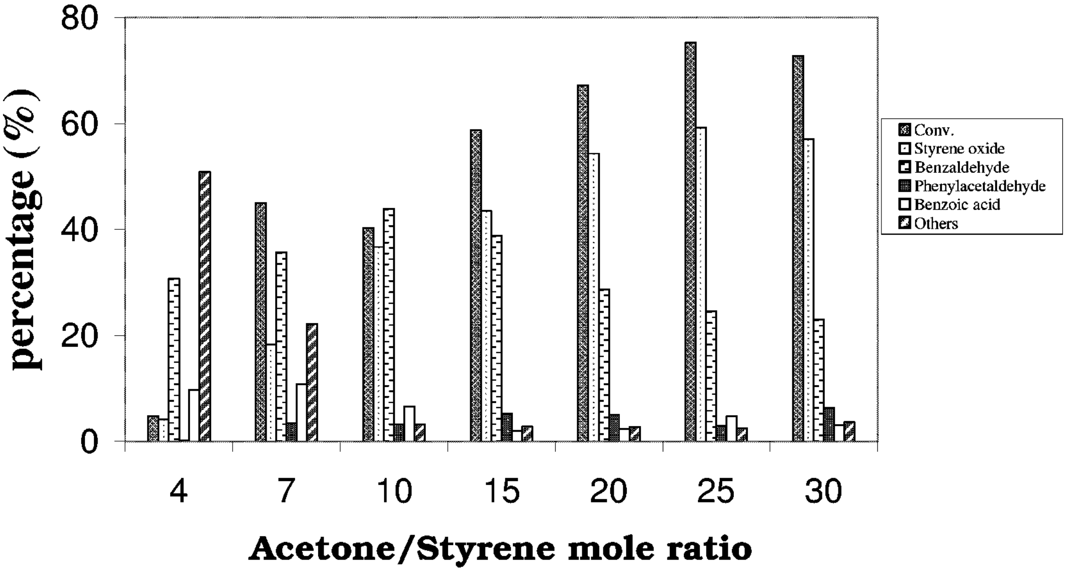

Figure 1. Influence of acetone/styrene mole ratio on styrene epoxidation. Reaction conditions: temperature 373 K, pressure 200 psi, time 30 min, styrene/TBHP mole ratio = 12 and catalyst (V-FER) = 0.05 g.

Table 2

Effect of solvents on styrene epoxidation.[a]

Solvent	Styrene conv. (%)	Product distribution selectivity[b] (%) B	SO	PA	BA	O
Cyclohexane	57.0	45.44	48.07	4.74	1.23	0.35
Acetonitrile	58.0	38.62	51.38	3.03	2.17	2.24
Acetone	75.3	24.57	59.18	2.92	4.72	2.52

[a] Reaction conditions: time 30 min; styrene/TBHP mole ratio = 12; solvent/styrene mole ratio = 25; catalyst (V-FER) = 0.05 g (Si/V = 20); temperature 373 K; pressure 200 psi.

[b] B = benzaldehyde; SO = styrene oxide; PA = phenylacetaldehyde; BA = benzoic acid; O = other unidentified high boilers and polymers.

Table 3

Effect of temperature on styrene epoxidation.[a]

Temperature (°C)	Styrene conv. (%)	Product distribution selectivity[b] (%) B	SO	PA	BA	O
353	63.9	30.05	49.14	5.01	1.41	2.82
373	75.3	24.57	59.18	2.92	4.72	2.52
393	82.1	43.01	33.01	5.85	9.78	6.21

[a] Reaction conditions: pressure 200 psi; time 30 min; styrene/TBHP mole ratio = 12; solvent/styrene mole ratio = 25; catalyst (V-FER) = 0.05 g (Si/V = 20); (solvent acetone).

[b] B = benzaldehyde; SO = styrene oxide; PA = phenylacetaldehyde; BA = benzoic acid and O = other unidentified high boilers and polymers.

and that for benzaldehyde decreased. At high pressure the styrene oxide formed may be rapidly isomerizing to phenylacetaldehyde.

3.4. Effect of different transition metal substituted molecular sieves on styrene epoxidaton

Table 4 summarizes the effect of different transition metal substituted metallosilicate molecular sieves for styrene epoxidation. Vanadosilicates with two different Si/V ratios were investigated. The conversion of styrene increased with the increase in Si/V ratio. This may be due to well-dispersed vanadium ions in the FER structure in the case of V-FER (HR). Even though V-FER (HR) with $SiO_2/V_2O_5 = 120$ was found to give higher conversion, Ti-FER ($SiO_2/TiO_2 = 114$) exhibited higher selectivity for styrene oxide. Under similar reaction conditions, TS-1 was found to give benzaldehyde as major product along with low yield of styrene oxide, however, Ti-FER exhibited better selectivity for styrene oxide. This may be related to structural differences of FER and TS-1 type molecular sieves. In the case of the vanadium impregnated sample a marked increase in conversion was observed, however, the selectivity for styrene oxide decreased significantly, yielding higher

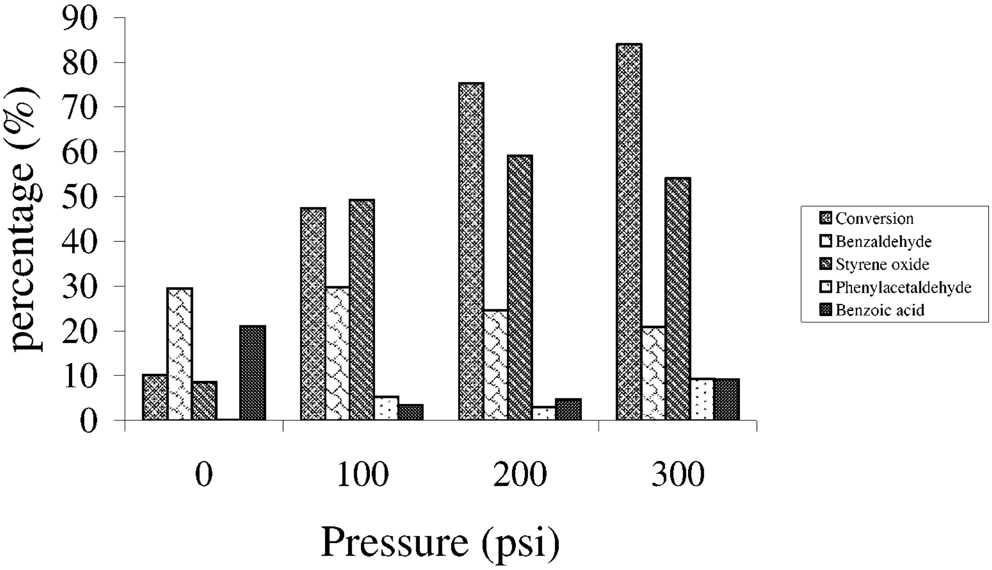

Figure 2. Influence of pressure on styrene epoxidation. Reaction conditions: temperature 373 K, time 30 min, styrene/TBHP mole ratio = 12, acetone/styrene ratio = 25 and catalyst (V-FER) = 0.05 g.

Table 4
Effect of different transition metal substituted metallosilicate molecular sieve zeolites for styrene epoxidation.[a]

Catalyst	Styrene conv. (%)	Product distribution selectivity[b] (%) B	SO	PA	BA	O
V-FER (LR)	75.3	24.57	59.18	2.92	4.72	2.52
V-FER (HR)	85.5	27.75	52.43	9.32	3.57	2.4
Ti-FER	76.5	24.31	57.42	7.97	2.48	1.83
TS-1	84.7	38.02	24.56	27.86	3.78	2.48
V-impregnated Si-FER	94.7	45.13	7.39	7.91	5.43	29.99[c]
Fe-FER	87.0	33.79	17.25	13.46	7.64	20.85
V-FER[d]	60.0	37.5	10.17	3.5	7.83	36.67[c]
–[e]	23.3	40.77	3.61	3.43	9.58	41.46
–[f]	99.2	26.21	3.33	0.71	12.1	50.32

[a] Reaction conditions: temperature 373 K; pressure 200 psi; time 30 min; styrene/TBHP mole ratio = 12; acetone/styrene mole ratio = 25; catalyst = 0.05 g.

[b] B = benzaldehyde; SO = styrene oxide; PA = phenylacetaldehyde; BA = benzoic acid and O = other unidentified high boilers and polymers.

[c] Lower boilers: benzene, toluene.

[d] Reaction carried out in the presence of N_2 atm and catalyst.

[e] Reaction carried out in the absence of catalyst and in presence of N_2 atm.

[f] Reaction carried out in the absence of catalyst.

amount of low and high boilers including polymers. This indicates that surface vanadium is not selective. Fe-FER showed higher conversion but poor selectivity for styrene oxide and the major products were benzaldehyde, high boilers and polymers, indicating Fe-FER is active but not selective for epoxidation. It is known that styrene epoxidation with molecular oxygen alone gives 50% conversion with selectivity ratio for benzaldehyde and styrene oxide of 1 : 1 [17].

When the reaction was carried out in nitrogen atmosphere with TBHP as the oxidant the conversion was about 60% with lower boilers as major constituents (~34%). The above results indicate that molecular oxygen plays an important role in this reaction. Furthermore, when the above reaction was carried out in the absence of a catalyst the conversion decreased (~23%) and benzaldehyde and polymers are the major products. The reaction is also carried out in the presence of air and in the absence of catalyst (373 K, 200 psi), in which case conversion is almost 100% with 50% of polymers. This shows that the presence of catalyst increases the selectivity for styrene oxide.

4. Conclusion

(1) V-FER and Ti-FER are active and selective in styrene epoxidation.

(2) The optimum reaction parameters for the production of styrene oxide in the presence of an initiator and a solvent/styrene (molar ratio) of 25 are 373 K (temperature) and 200 psi (pressure).

(3) Solvent dilution and solvent polarity are essential in increasing the conversion and selectivity for styrene oxide.

(4) Presence of a catalyst suppresses the side reactions such as the formation of benzaldehyde and the isomerization of styrene oxide to phenylacetaldehyde.

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