Selectively catalytic epoxidation of styrene with dry air over the composite catalysts of Co-ZSM-5 coordinated with ligands

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Abstract

The catalytic activity of composite catalysts of Co-ZSM-5 coordinated with ligands for the selective epoxidation of styrene with dry air was studied in the temperature range of 50–100 °C under atmospheric pressure. The catalyst Co-ZSM-5(L_2) containing vanillic aldehyde salicylhydrazone (L_2) exhibited the best activity and selectivity for the epoxidation; e.g. 96.9 mol% of styrene conversion with an epoxide selectivity of 94.0% as well as a low benzaldehyde selectivity of 3.1% was attained when the concentration of styrene in solvent was 0.2 mmol/g. Over the composite catalysts of Co-ZSM-5 coordinated with ligands, the overall selectivity of the epoxide (styrene oxide) plus the corresponding isomer (phenylacetaldehyde) was higher than 90%. It is noteworthy that the use of TBHP in small amounts efficiently initiated the reaction, and the lack of TBHP led to a low conversion and selectivity.
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Keywords: Styrene epoxidation; Zeolite composite catalyst; Ligand; Air; Co-ZSM-5

1. Introduction

The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals, since epoxides are key starting materials for a wide variety of products [1–3]. The catalytic systems that have been reported useful for the oxidation of olefinic compounds include Mn (III) (salen) complexes in homogeneous media [4–6], Mn (III) (bipyridine) complex cations immobilized on Al-MCM-41 [7], Mn (III) (salen) complexes encapsulated in zeolite-X [8], Mo- or Ti-containing mesoporous MCM-41 [9], Ru (II) complexes containing pyridine and picoline ligands [10], titanium silicate molecular sieves [11,12], and heteropoly tungstate [13].

Recently, the catalytic epoxidation with hydroperoxides (including organic peroxides and hydrogen peroxide), oxygen and air as oxidants has become an especially attractive target. Among those processes, the TS-1/H_2O_2 catalytic system [14–16] has been regarded as the most successful one, in which TS-1 exhibits high activity and selectivity under mild conditions,

and the use of H_2O_2 produces water as the only by-product, so that this process is regarded as a green technology. However, compared with molecular oxygen or air, the relatively high cost of H_2O_2 severely hinders its wide applications in catalytic oxidations. More and more chemical researchers tend to pursue new oxidation processes using molecular oxygen or naturally cheap air as the oxidant. But, since triplet ground state of O_2 disfavors reactions with singlet organic compounds, the controllable activation of molecular oxygen is a serious challenge. In addition, finding a path for the selective oxidation of organic feedstock using dioxygen can assist the improvements in the management of our natural resources.

Epoxyethylbenzene is an important raw material for the manufacturing of β-phenethy alcohol, tetramisole, levamisole and phenylacetaldehyde, which have found extensive applications in the industries of petrochemicals, fine chemicals, medicines, perfumery and polymers. Traditionally, epoxyethylbenzene was obtained by the epoxidation of styrene with oxyhalides (or from chlorohydrins and bromohydrins via dehalogenation/dehydration under basic conditions); however, these procedures produced a great deal of environmentally undesirable wastes. It is highly desirable to develop an environmentally benign procedure.

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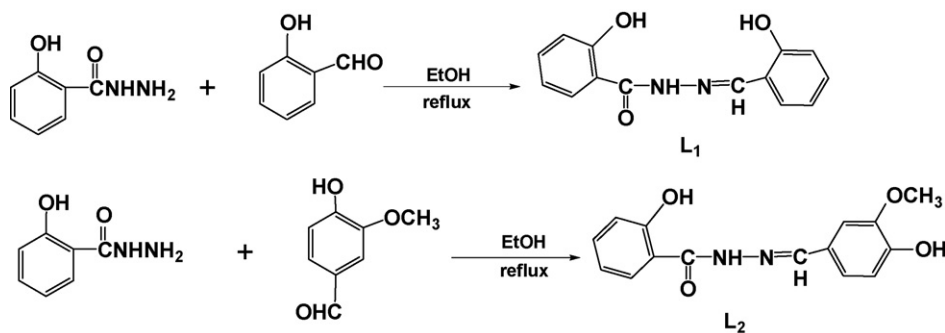
Scheme 1. Synthetic routes and structures of **L₁** and **L₂**.

Recently, Wang and co-workers [17] reported that Co²⁺-exchanged faujasite zeolites could catalyze the epoxidation of styrene with O₂; Co-MCM-41 and Co-X clearly showed higher efficiency than either Co₃O₄ oxide or Co²⁺ ions in the liquid phase. Actually, earlier on Spadlo et al. [18] developed the non-catalytic aerobic oxidation of styrene with 44.3% selectivity of epoxide, in which PhCMe₂OOH was used as a free-radical initiator to initiate the characteristic free-radical reactions between styrene and molecular oxygen. It has been reported that the composite catalyst consisting of *cis*-MoO₂(solv) salicylidene salicyloylhydrazine and zeolite-Y resulted in an epoxide selectivity of 68% using oxygen as the oxidant [19]. Co-ZSM-5 and Cu-ZSM-5 have been used in the selective catalytic reduction of nitrogen oxide by methane (SCR–deNOx reaction) and petro-chemical industry [20]. However, to date, no study has been focused on the catalytic activity of Co-ZSM-5 for the epoxidation of alkenes with air.

In the present study, two schiff-base ligands salicyldehyde salicylhydrazone (**L₁**) and vanillic aldehyde salicylhydrazone (**L₂**) were synthesized, as depicted in Scheme 1. Subsequently, both ligands were coordinated with Mn-Y, Mo-Y, Co-Y, Co-ZSM-5, Co-4A and Co-3A to yield several zeolite composite catalysts, which were first used in the epoxidation of styrene with dry air. It was observed that the Co-ZSM-5(**L₂**) catalyst showed an excellent catalytic activity for the epoxidation of styrene with air at 90 °C in the presence of TBHP as the initiator.

2. Experimental

2.1. Materials

The main reagents used in the synthesis of schiff-base ligands and catalysts were salicylic acid hydrazide (99%), salicylade-hyde (99.5%), vanillic aldehyde (99.5%), manganese(II) acetate tetrahydrate (Mn(Ac)₂·4H₂O, 99%), cobalt(II) acetate tetrahy-drate (Co(Ac)₂·4H₂O, 99.5%), ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, 99.5%), molecular sieves (Na-Y, Na-ZSM-5, 4A, 3A), pyridine (99%), dimethyl sulfoxide (DMSO, 98%) and absolute ethanol (EtOH, 99.5%). The freshly distilled solvents were dimethylacetamide (DMA), dimethylformamide (DMF), *n*-hexane, acetone, and cyclohexanone. Other reagents included distilled water, styrene (>99%), oxygen, aqueous *tert*-butyl hydroperoxide (TBHP, >65%) and dry air.

2.2. Synthesis of schiff-base ligands

2.2.1. Salicyldehyde salicylhydrazone (**L₁**)

The salicylic acid hydrazide (0.03 mol, 4.56 g) was added into a 100 ml round-bottom flask filled with 40 ml of absolute ethanol under stirring, and then the mixture was refluxed at 80 °C until the dissolution of salicylic acid hydrazide. After 3.4 ml of salicylaldehyde was slowly dropped into the above solution, the resulting mixture was again refluxed for 3 h until the completion of reaction (checked by TLC), which was then cooled down to the room temperature. A coarse product was recovered by fil-tration, which was further re-crystallized from a mixed solvent of ethanol and dimethyl formamide to obtain pure yellowish crystal ligand (**L₁**) with a yield of 91.0%. M.p.: 274 °C; IR (KBr) (cm⁻¹): 3244, 3223, v (N–H); 1637, 1622, v (C=O); 1597, 1560, 1490, 1488, v (C=N); ¹H-NMR (DMSO-d_6) (600 MHz): 12.031(s, 1H, Ar–OH), 11.709(m, 1H, N–H), 11.281(m, 1H, Ar–OH), 8.725(m, 1H, N=C–H), 7.412–6.964(m, 8H, Ar–H).

2.2.2. Vanillic aldehyde salicylhydrazone (**L₂**)

While stirring salicylaldehyde (0.03 mol, 4.56 g) and vanillic aldehyde (0.03 mol, 4.56 g) were added into a 100 ml round-bottom flask filled with 40 ml of absolute ethanol, which was then refluxed at 80 °C for 3 h until the completion of reac-tion (checked by TLC). Thereafter, the solvent was removed by a rotary evaporator to give a creamy compound, which was further re-crystallized from a mixed solvent of acetone and dimethylformamide to produce pure yellowish crystal lig-and **L₂** with a yield of 85%. M.p.: 205 °C; IR (KBr) (cm⁻¹): 3278, 3260, v (N–H); 1645, 1634, v (C=O); 1615, 1611, 1530, 1521, v (C=N); ¹H-NMR (DMSO-d_6) (600 MHz): 11.972(m, 1H, Ar–OH), 11.710(m, 1H, N–H), 9.62(m, 1H, Ar–OH), 8.173(m, 1H, N=C–H), 7.433–6.864 (m, 7H, Ar–H), 3.982(s, 3H, –OCH₃).

2.3. Preparation of zeolite composite catalysts

Initially, ion exchange was carried out by stirring 5 g of molecular sieve (Na-Y, Na-ZSM-5, 4A or 3A) in an aqueous solution (250 ml) of ammonium molybdate (0.18 g, 0.17 mmol) (or cobalt(II) acetate tetrahydrate (0.3 g, 1.2 mmol), or man-ganese(II) acetate tetrahydrate (0.29, 1.2 mmol)) at 90 °C for 9–10 h. The powder was then recovered by filtration, washed

several times with distilled water and dried in an oven at 120 °C for 5 h. Above ion-exchanged zeolites were separately added to hot ethanolic solution of L_1 (0.256 g, 1 mmol) or L_2 (0.286 g, 1 mmol), and allowed to react with stirring at 80 °C for 10 h to ensure the formation of composites. In order to remove the excess ligand from the surface of zeolite, the recovered solids that had been washed several times with hot ethanol were subjected to the Soxhlet extraction under refluxing in ethanol until no free ligand was detected from the extract by the UV spectrum. The resulting zeolite composites coordinated with ligands were in vacuo dried at 80 °C for 24 h and stored in the desiccator for catalytic uses.

2.4. Structural characterizations of L_1, L_2, Co-ZSM-5(L_1) and Co-ZSM-5(L_2)

The XRD (X-ray diffraction) patterns of solid samples were recorded on a Rigaku D/MAX–IIIC diffractometer with Cu Kα ($\lambda = 1.54184$ Å) radiation operating at 30 kV and 25 mA. The scanning range was from $2\theta = 5$ to $65°$ with a scanning speed of $2°$/min. Melting point of the ligand was determined by a Shimadzu DSC-60 instrument (differential scanning calorimeter) in the range of room temperature 400 °C. IR spectra (KBr pellets) were recorded on a Shimadzu IR Prestige-21 Fourier Transform Infrared spectrometer. UV–vis spectra of samples were determined on a Shimadzu UV-2550 spectrometer. ^{1}H-NMR spectra (600 MHz) of samples dissolved in DMSO-d_6 were measured on a Varian Inova-600 (600 MHz) NMR instrument using 0.03% TMS ((CH$_3$)$_4$Si) as an internal standard. Metal-containing zeolites were determined by chemical analysis to contain 1.2 wt.% Mo for Mo-Y, 1.1 wt.% Mn for Mn-Y and 1.3 wt.% Co for Co-Y, 1.1 wt.% Co for Co-4A, 1.0 wt.% Co for Co-3A and 1.2 wt.% Co for Co-ZSM-5.

2.5. Epoxidation of styrene

2.5.1. Epoxidation of styrene with TBHP, O_2, air and air + TBHP over Co-ZSM-5(L_2)

Ten grams of solvent (DMF), 0.1 g of Co-ZSM-5(L_2), 3 mmol of styrene and 3 mmol of TBHP (or dry air with a flow rate of 30 ml/min, or oxygen with a flow rate of 12 ml/min, or dry air with a flow rate of 30 ml/min plus 0.05 mmol of TBHP as the initiator) were heterogeneously mixed in a 50 ml three-necked flask equipped with a cooling-water condenser under magnetic stirring and heated to 90 °C. Each reaction was continued for 5 h prior to GC determination.

2.5.2. Epoxidation of styrene with air + TBHP over composite catalysts

In unspecilized cases, the catalyst (0.1 g), appropriate amount of styrene, 10 g of solvent (DMF) and 0.05 mmol of TBHP were mixed in a 50 ml three-necked flask equipped with a cooling-water condenser and with an air pump under magnetic stirring and heated to desired temperatures. Then dry air with a stable flow rate of 30 ml/min controlled by a flowmeter was introduced by bubbling into the bottom of reactor at atmospheric pressure. Each reaction was continued for 5 h prior to GC determination.

2.5.3. GC analysis of products

The quantitative GC analysis of the epoxidized products was performed by a GC-900A equipped with an FID detector and a SUPELCO BETA-DEX^{TM} 120 capillary column (30 m × 0.25 mm × 0.25 μm). Hydrogen was used as carrier gas. GC error for the determination was within ±3%. The products include epoxyethylbenzene (epoxide), benzaldehyde (Bena), phenylacetaldehyde (Phea), and benzoic acid + phenylacetic acid (other).

3. Results and discussion

3.1. Characteristics of catalysts

XRD patterns of calcined ZSM-5 and dried Co-ZSM-5 samples are recorded, where one can observe characteristic diffractions of ZSM-5 lattice emerging at $2\theta = 7.87°$, 8.79°, 23.11°, 23.79° and 24.39°, typical of MFI topology. Co-containing ZSM-5 prepared by ion-exchange at 363 K and drying at 393 K maintains an integrated ZSM-5 framework, without detectable diffraction peaks of metal ions. The IR vibration spectrum of dried Co-ZSM-5 further proves the integrity of ZSM-5 framework of the sample that underwent the treatments of ion-exchange and drying.

IR spectra of L_1, L_2, Co-ZSM-5, Co-ZSM-5(L_1) and Co-ZSM-5(L_2) are presented in Fig. 1. For as-prepared ligand L_1, absorbance bands attributed to C=O at 1655, 1562 and 1232 cm^{-1}, C=N at 1636 cm^{-1}, C–O at 1157 cm^{-1}, O–H at 3030 cm^{-1} and N–H at 3420 cm^{-1} appear. In addition, a strong band found at 1622 cm^{-1} is attributed to C=N–N=C, group. This IR evidence has been registered earlier for a similar class of ligands that behave as tridentate dibasic ligands upon enolization
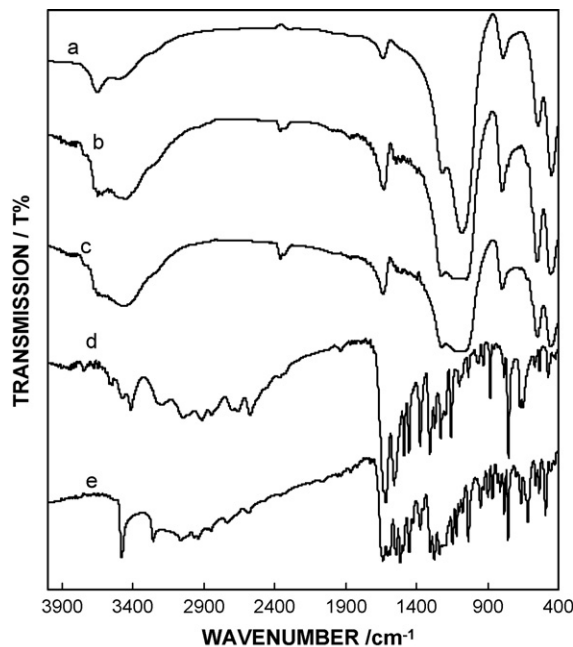

Fig. 1. IR spectra of different solid samples: (a) Co-ZSM-5, (b) Co-ZSM-5(L_1), (c) Co-ZSM-5(L_2), (d) L_1 and (e) L_2.
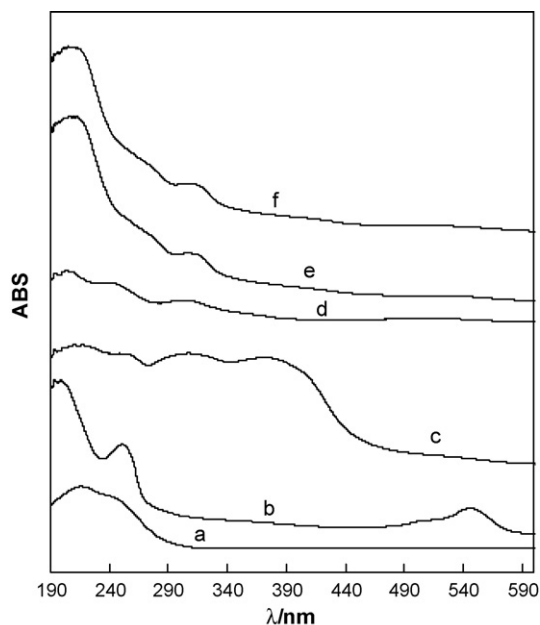
Fig. 2. UV–vis spectra of solid samples: (a) ZSM-5, (b) Co-ZSM-5, (c) Co-ZSM-5(L_1), (d) Co-ZSM-5(L_2), (e) recovered Co-ZSM-5(L_1) and (f) recovered Co-ZSM-5(L_2).

Table 1
Effect of various zeolite composite catalysts on the epoxidation of styrene

Catalyst	Styrene conversion (mol%)	Selectivity (%)			
		Epoxide	Bena	Phea	Other
Mo-Y(L_1)	15.7	65.2	34.8	0	0
Mo-Y(L_2)	16.5	68.0	31.2	0	0.8
Mn-Y(L_1)	36.7	67.2	30.1	2.0	0.7
Mn-Y(L_2)	38.1	70.3	27.9	1.6	0.2
Co-Y(L_1)	38.3	72.2	26.3	0.5	1.0
Co-Y(L_2)	41.6	74.3	23.9	0.6	1.2
Co-3A(L_1)	80.8	81.8	6.1	4.4	7.7
Co-3A(L_2)	85.1	87.1	8.1	3.7	1.1
Co-4A(L_1)	83.7	79.2	5.9	3.2	10.6
Co-4A(L_2)	87.9	80.7	5.3	4.8	9.5
Co-ZSM-5(L_1)	88.2	87.8	5.3	4.4	2.5
Co-ZSM-5(L_2)	91.8	90.1	4.6	4.2	1.1
Co-ZSM-5	67.3	78.5	11.2	5.6	4.7

Reaction conditions: solvent, DMF (10 g); TBHP, 0.05 mmol; catalyst, 0.3 g; temperature, 363 K; time, 5 h; flow rate of air (30 ml/min).
Bena, benzaldehyde, Phea, phenylacetaldehyde, other, benzoic acid + phenyl-acetic acid.

[21]. For the ligand L_2, absorbance bands attributed to C=O at 1638, 1633, 1525 and 1516 cm^{-1}, C=N at 1610 and 1606 cm^{-1}, C–O at 1241, 1277, 1236 and 1150 cm^{-1}, O–H at 3265 cm^{-1} and N–H at 3481 cm^{-1} appear. For Co-ZSM-5, Co-ZSM-5(L_1) and Co-ZSM-5(L_2), except for similar infrared framework vibrations observed at 1236, 1103, 806, 553, and 460 cm^{-1}, both Co-ZSM-5(L_1) and Co-ZSM-5(L_2) show additional infrared signals in the range of 1600–1450 and 2900–3550 cm^{-1}, which can be associated with the ligand molecules coordinated on the surface of Co-ZSM-5. This coordination also leads to the emergence of a weak infrared band at 630 cm^{-1}, attributed to Co-N, for Co-ZSM-5(L_1) and Co-ZSM-5(L_2).

UV–vis spectra of six ZSM-5 composite samples are shown in Fig. 2. Clearly, there are recognizable four bands at 258, 289, 313 and 333 nm for L_1, four bands at 268, 318, 331 and 364 nm for L_2, a broad band at 225 nm for ZSM-5, three bands at 220, 256 and 553 nm for Co-ZSM-5, four bands at 217, 251, 312 and 384 nm for Co-ZSM-5(L_1), three bands at 210, 245 and 310 nm for Co-ZSM-5(L_2), three bands at 215, 271 and 310 nm for reused Co-ZSM-5(L_1), and three bands at 213, 269 and 310 nm for reused Co-ZSM-5(L_2). This characterization further reveals the coordination of organic ligand molecules and the formation of new bonds on the surface of Co-ZSM-5. For example, once ligands L_1 and L_2 are coordinated on Co-ZSM-5, two ultraviolet signals at 220 and 256 nm of Co-ZSM-5 shift to 217 and 251 nm for Co-ZSM-5(L_1), and to 210 and 245 nm for Co-ZSM-5(L_2); meanwhile the ultraviolet signal at 553 nm of Co-ZSM-5 disappears, followed by the emergence of two new UV signals at 312 and 318 nm for Co-ZSM-5(L_1) and a new signal at 310 nm for Co-ZSM-5(L_2). In addition, we can observe an apparent change from the pink color of Co-ZSM-5 to the flavescent color of Co-ZSM-5(L_1), and to the white color of Co-ZSM-5(L_2).

3.2. Epoxidation of styrene with air + TBHP over different catalysts

When no catalyst was added, only 10.7 mol% of styrene was converted into the products inclusive of epoxide (63.4% of selectivity) and benzaldehyde (36.6% of selectivity). When cobalt acetate was used, the conversion of styrene slightly increased to 25.5 mol% with an epoxide selectivity of 56.2%. Table 1 presents the effect of different zeolite composite catalysts on the epoxidation of styrene, in which the reactions were conducted at 363 K using DMF as the solvent and TBHP as the initiator. Very clearly, the catalytic activity of those catalysts gradually decreased in the sequence of Co-ZSM-5(L_2) > Co-ZSM-5(L_1) > Co-4A(L_2) > Co-3A(L_2) > Co-4A(L_1) > Co-3A(L_1) > Co-Y(L_2) > Co-Y(L_1) ≈ Mn-Y(L_2) > Mn-Y(L_1) > Mo-Y(L_2) ≈ Mo-Y(L_1), while the epoxide selectivity reduced in the order of Co-ZSM-5(L_2) > Co-ZSM-5(L_1) ≈ Co-3A(L_2) > Co-4A(L_2) ≈ Co-4A(L_1) ≈ Co-3A(L_1) > Co-Y(L_2) > Co-Y(L_1) > Mn-Y(L_2) > Mn-Y(L_1) ≈ Mo-Y(L_2) > Mo-Y(L_1). Within 5 h, the conversion of styrene had reached 88.2–91.8 mol% over Co-ZSM-5(L_2) and Co-ZSM-5(L_1), approximately 8.24–8.57 times that of the blank reaction. Co-4A(L_2) and Co-4A(L_1) catalyzed 83.7–87.9 mol% of styrene conversion, while 80.8–85.1 mol% of conversion was realized on Co-3A(L_1) and Co-3A(L_2). Comparatively, all the Y zeolite composite catalysts merely achieved relatively low conversions of styrene, which were 36.7–38.1 mol% on Co-Y(L_1) and Co-Y(L_2), 38.3–41.6 mol% on Mn-Y(L_1) and Mn-Y(L_2), 15.7–16.5 mol% on Mo-Y(L_1) and Mo-Y(L_2), where the latter was comparable to that reported for the composite catalyst consisting of cis-MoO$_2$(solv) salicylidene salicyloylhydrazine and zeolite-Y [19]. Under identical conditions, the selectivity to epoxide reached 87.8–91.1% over Co-ZSM-5(L_2) and Co-ZSM-5(L_1), 81.8–87.1% over Co-3A(L_1) and Co-3A(L_2), 79.2–80.7% over Co-4A(L_2) and Co-4A(L_1), respectively; however, Co-Y(L_1), Co-Y(L_2), Mn-Y(L_1), Mn-Y(L_2), Mo-Y(L_1) and Mo-Y(L_2)

Table 2
Effect of various oxidants on the epoxidation of styrene

Oxidant	Styrene conversion (mol%)	Selectivity (%)			
		Epoxide	Bena	Phea	Others
TBHP[a]	37.2	69.4	30.6	0	0
Air[b]	7.0	31.5	68.5	0	0
O_2[c]	27.2	45.6	43.8	0	10.6
Air + TBHP[d]	90.5	91.1	3.7	4.0	1.2

Reaction conditions: solvent, DMF (10 g); catalyst, Co-ZSM-5(**L2**) (0.1 g); temperature, 363 K; time, 5 h.

[a] 3 mmol of TBHP.
[b] Flow rate of air (30 ml/min).
[c] Flow rate of oxygen (12 ml/min).
[d] Flow rate of air (30 ml/min) and TBHP (0.05 mmol).

resulted in lower epoxide selectivities of 65.2–74.3%, higher than 63.4% of the blank reaction.

The overall selectivity of both cleaved and deeply-oxidized by-products consisting of benzaldehyde, benzoic acid, and phenylacetic acid varied in the range of 25.1–34.8% over six M-Y(**L**) catalysts inclusive of Co-Y(**L1**), Co-Y(**L2**), Mn-Y(**L1**), Mn-Y(**L2**), Mo-Y(**L1**) and Mo-Y(**L2**), which decreased to 13.8–16.5% on Co-3A(**L1**), Co-4A(**L1**) and Co-4A(**L2**), and further decreased to 5.7–9.2% on Co-3A(**L2**), Co-ZSM-5(**L2**) and Co-ZSM-5(**L1**). Especially, the overall selectivity of above-mentioned by-products was the lowest (only 5.7%) on Co-ZSM-5(**L2**), accompanied with 94.3% of the overall selectivity of the desired epoxide and its isomer (phenylacetaldehyde). Obviously, M-Y(**L**) did not behave as efficient catalysts for the reaction, while Co-ZSM-5(**L**), and Co-3A(**L2**) outstandingly promoted the epoxidation of styrene with air under the initiation of TBHP. Especially Co-ZSM-5(**L2**) achieved the highest conversion of styrene (91.8 mol%) and the best selectivity of epoxide (90.1%), showing the efficiency of Co-ZSM-5(**L**) composite catalysts for the epoxidation to form the epoxide. It is noteworthy that Co-ZSM-5 without any ligand catalyzed only 67.3 mol% of styrene conversion, with the yield of 78.5% epoxide, 11.2% benzaldehyde, 5.6% phenylacetalde-hyde, and 4.7% benzoic acid + phenylacetic acid under identical experimental conditions. Possibly, the use of the ligand could affect the formation of free radicals that favor the yield of epoxide instead of other products through varying the steric coordination environment of solvent, O_2 and styrene on the catalyst.

3.3. Epoxidation of styrene with various oxidants over Co-ZSM-5(L2)

Table 2 compares the effect of various oxidants on the epoxidation of styrene catalyzed by Co-ZSM-5(**L2**) under identical conditions. When only TBHP was used as the oxidant, the conversion of styrene was 37.2 mol% in 5 h, with an epoxide selectivity of 69.4%. Without the addition of TBHP, dry air oxidized 7.0 mol% of styrene at 363 K, and pure O_2 converted 27.2 mol% of styrene in 5 h; however, in both cases the selectivity of both benzaldehyde and deeply-oxidized acids was high (up to 54.4–68.5%). Once the TBHP initiator in small
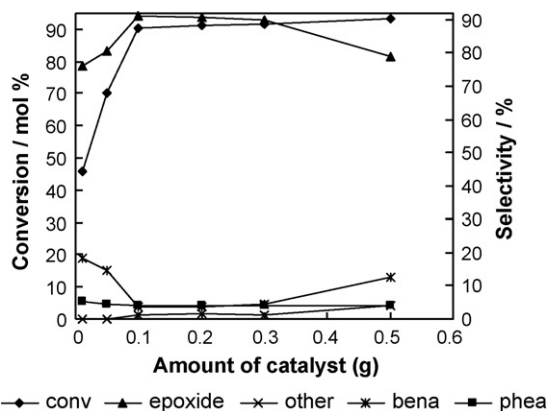

Fig. 3. Effect of the catalyst amount (Co-ZSM-5(**L2**)): styrene, 3 mmol; DMF, 10 g; TBHP, 0.05 mmol; flow rate of air, 30 ml/min; temperature, 363 K; time, 5 h.

amounts was added into the catalytic system using dry air as the oxidant, the conversion of styrene and the selectivity of epoxide were remarkably elevated to 90.5 mol% and 91.1%, with the low yield of 3.7% benzaldehyde, 4.0% of phenylacetaldehyde and 1.2% of other by-products. The results further indicate the efficiency of this catalytic system for the selective epoxidation of styrene with air.

3.4. Factors influencing the catalytic activity of Co-ZSM-5(L2)

3.4.1. Effect of the catalyst amount and various solvents

The effect of the catalyst amount on the epoxidation is illustrated in Fig. 3. When the amount of Co-ZSM-5(**L2**) was increased from 0.01 to 0.5 g, the conversion of styrene showed a gradual increase from 45.9 to 93.2 mol%. However, the selectivity of epoxidation showed an increase from 76.3 to 91.1% as the amount of Co-ZSM-5(**L2**) was increased from 0.01 to 0.1 g, and then it gradually decreased from 91.1 to 84.2% with continuously increasing amount of Co-ZSM-5(**L2**) from 0.1 to 0.5 g.

Table 3 presents the effect of various solvents on the epoxidation of styrene with air catalyzed by Co-ZSM-5(**L2**), in which the tested solvents included DMF, DMA, cyclohexanone and pyridine. Under our experimental conditions, the conversion of styrene could be arranged in the ascending order of pyridine (0) < DMA (35.9 mol%) < cyclohexanone (50.3 mol%) < DMF (90.5 mol%), closely consistent with the rising order of the epox-

Table 3
Effect of various solvents on the epoxidation of styrene

Solvent	Styrene conversion (mol%)	Selectivity (%)			
		Epoxide	Bena	Phea	Others
DMF	90.5	91.1	3.7	4.0	1.2
DMA	35.9	70.5	26.6	0	2.9
Cyclohexanone	50.3	82.3	16.5	1.2	0
Pyridine	0	0	0	0	0

Reaction conditions: solvent, 10 g; TBHP, 0.05 mmol, catalyst, Co-ZSM-5(**L2**) (0.1 g); temperature, 363 K; time, 5 h; flow rate of air, 30 ml/min.
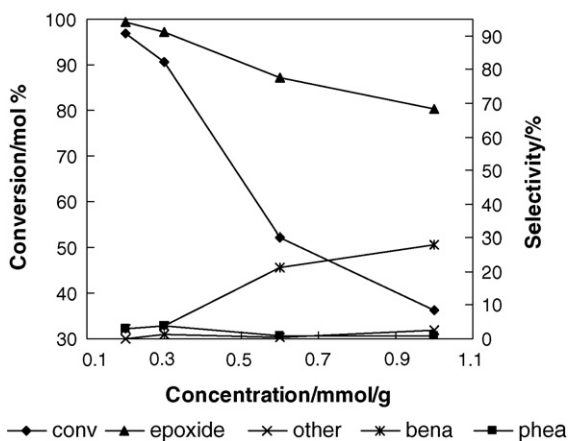
Fig. 4. Effect of the substrate concentration: DMF, 10 g; Co-ZSM-5(L₂), 0.1 g; TBHP, 0.05 mmol; flow rate of air, 30 ml/min; temperature, 363 K; time, 5 h.

ide selectivity: pyridine (0) < DMA (70.5%) < cyclohexanone (82.3%) < DMF (91.1%). The addition of basic pyridine (pH 9–10) totally inhibited styrene from being oxidized with air, while DMF (pH 6–7) promoted highly selective epoxidation of styrene. Low efficiency of DMA solvent could be due to larger steric hindrance of the intermediate coordination states.

3.4.2. Effect of the styrene concentration, the reaction time and temperature

Fig. 4 exhibits the effect of substrate concentration on the epoxidation of styrene over Co-ZSM-5(L₂), in which the reactions were conducted at 363 K using DMF as the solvent. When the amount of styrene in 10 g of solvent was increased from 2 to 6 mmol, the conversion of styrene showed a gradual decrease from 96.9 to 52.3 mol%, accompanied with a reduction of the epoxide selectivity from 94.0 to 77.6%. With a continuous increase in the amount of styrene in 10 g of solvent to 10 mmol, the conversion of substrate and the selectivity of epoxide continued to reduce to 36.2 mol% and 68.4%, respectively. The selectivity of main cleaved by-propducts (benzaldehyde + other) kept an increase from 6.0 to 31.6%. When the amount of styrene in 10 g of solvent was 3 mmol, the selectivity of epoxide reached 91.1%, with a substrate conversion of 90.5 mol%, which was used as an optimal condition unless specialized.

The impact of reaction temperature on the epoxidation of styrene over Co-ZSM-5(L₂) is depicted in Fig. 5. Distinctly, the conversion of styrene stepwise increased with the reaction temperature: 323 < 333 < 343 < 353 < 363 K. For example, the conversion of styrene was 11.6 mol% at 323 K, slowly rose to 25.6 mol% at 333 K, and quickly increased to 74.9 mol% at 353 K and to 90.5 mol% at 363 K. But the conversion of styrene reduced to 75.0 mol% with a continuous increase in the reaction temperature to 373 K. The selectivity of epoxide followed up the regularity of the styrene conversion with the temperature, which first increased from 64.2% at 323 K to the maximum of 91.1% at 363 K, and then slightly reduced to 85.9% at 373 K. It seems that a suitable temperature favored the formation of epoxide.

We also investigated the effect of reaction time on the epoxidation of styrene over Co-ZSM-5(L₂) at 363 K, as shown in
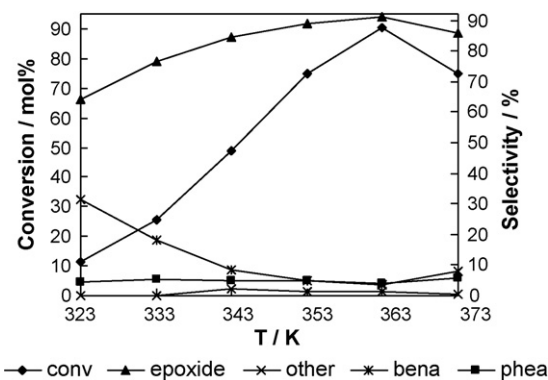

Fig. 5. Effect of the reaction temperature: styrene, 3 mmol; DMF, 10 g; Co-ZSM-5(L₂), 0.1 g; TBHP, 0.05 mmol; flow rate of air, 30 ml/min; time, 5 h.
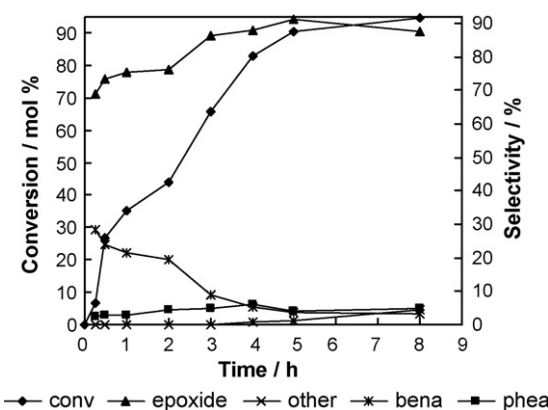

Fig. 6. Effect of the reaction time: styrene, 3 mmol; DMF, 10 g; Co-ZSM-5(L₂), 0.1 g; TBHP, 0.05 mmol; flow rate of air, 30 ml/min; temperature, 363 K.

Fig. 6. When the reaction time was zero, the conversion of styrene was zero. Within the reaction time of 15 min the conversion of styrene was about 6.8 mol%, and gradually increased to 26.6 mol% in 30 min, to 35.5 mol% in 1 h, to 43.9 mol% in 2 h, to 90.5 mol% in 5 h and to 94.7 mol% in 8 h with prolonging reaction time, showing the induction period characteristic of radical reaction. However, the selectivity of epoxyethylbenzene (epoxide) was 68.9% in 15 min, 73.2% in 30 min, 76.2% in 2 h, increased to 88.0% in 4 h and to 91.1% in 5 h, and then slightly reduced to 87.4% in 8 h.
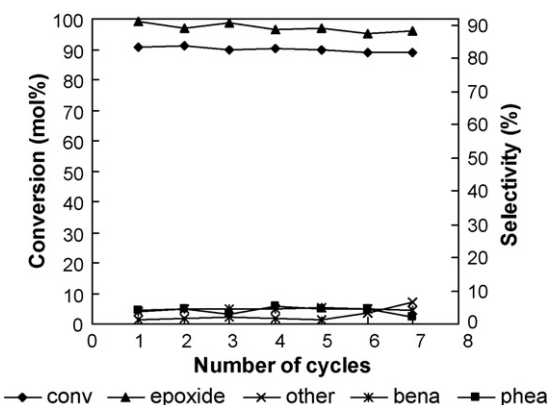

Fig. 7. Recycling studies of the catalyst Co-ZSM-5(L₂).

3.4.3. Recycling studies

Catalyst recycling experiments were carried out with repeated uses of Co-ZSM-5(L_2) at 363 K for 5 h. It can be seen from Fig. 7 that along with the reuse of Co-ZSM-5(L_2) (seven times) the conversion of styrene stepwise decreased from 90.9 to 88.9 mol%, while the selectivity of epoxide merely showed a small reduction from 91.1 to 88.3%. Chemical analyses of reaction mixture and the used catalysts did reveal the leaching of cobalt from Co-ZSM-5(L_2), for which about 8.3% of cobalt leached out in the former three recycles; i.e. the cobalt content reduced from 1.2 wt.% to ca. 1.1 wt.%. This may be due to the leaching of soluble Co species trapped in the pores of ZSM-5. For the latter four recycles, no leaching of cobalt was further detected; in this case the conversion of styrene and the selectivity of epoxide maintained more or less constant levels of about 89.5 mol% and 88.7%. This analysis further confirms the stability and recyclability of Co-ZSM-5(L_2).

Generally, the experimental results in the context have revealed the DMF-assisted epoxidation of styrene with air catalyzed by Co-ZSM-5(L_2) using TBHP (in small amount) as the initiator in the present system, where the addition of the latter actually assisted the improvement of substrate conversion and epoxide selectivity. The coordination between solvent and oxygen was further evidenced by UV spectra in Fig. 8, where two different experiments c (DMF + air) and d (DMA + air) gave two similar UV spectra. The introduction of air into the solvent resulted in the appearance of an electron-transition ultraviolet signal ranging from 270 to 285 nm associated with the electron transfer from oxygen to the electron-deficient carbonyl group in DMF or DMA, suggesting the coordination interaction between solvent and molecular oxygen, which may be an important step in the process of dissociating molecular oxygen to epoxidize styrene [17,19]. The relevant research in depth on the reaction

mechanism is still under way, and the result will be published elsewhere.

4. Conclusions

The schiff-base ligands derived from salicylic acid hydrazide were synthesized, and first coordinated with co-containing zeolites to prepare zeolite composite catalysts, which were characterised by XRD, IR, DSC, ^{1}H-NMR and UV–vis. The present work tested the activity of as-synthesized zeolite composites catalysts, especially of Co-ZSM-5(L_2), for the epoxidation of styrene with air under atmospheric pressure with TBHP in small amounts as the initiator, and investigated the factors influencing the conversion of styrene and the selectivity of epoxide. Zeolite composites catalysts could catalyze the occurrence of styrene epoxidation with air, in which the Co-ZSM-5(L_2) catalyst exhibited the best activity with 90.5 mol% of the substrate conversion and 91.1% of the epoxide selectivity for the concentration of 0.3 mmol styrene per gram solvent, as well as 96.9 mol% of styrene conversion with an epoxide selectivity of 94.0% and a low benzaldehyde selectivity of 3.1% for the concentration of 0.2 mmol styrene per gram solvent in 5 h under our experimental conditions. It is noteworthy that the experimental results revealed the DMF-assisted epoxidation of styrene with air catalyzed by Co-ZSM-5(L_2) using TBHP (in small amount) as the initiator in the present system. Recycling studies showed that Co-ZSM-5(L_2) was recyclable, and the leaching of cobalt from Co-ZSM-5(L_2) could be controlled in the range of <9%.

Fig. 8. UV spectra of liquid samples: (a) DMF; (b) DMA; (c) DMF + air; (d) DMA + air.

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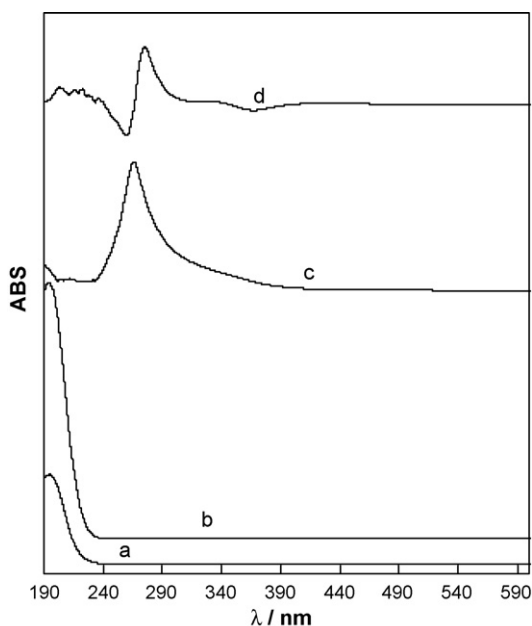[13] N. Mizumo, T. Hirose, R. Iwamoto, Stud. Surf. Sci. Catal. 84 (1994) 593.

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