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Co-ETS-10 and Co-AM-6 as active catalysts for the oxidation of styrene to styrene oxide and benzaldehyde using molecular oxygen

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ABSTRACT

Pristine ETS-10 and AM-6 and their Co^{2+} -exchanged forms were prepared, and their catalytic activities toward the oxidation of styrene in oxygen atmosphere were studied in dimethylformamide. The catalysts were denoted as Co-E10- n ($n = 0, 9, 26, 68, 81$) and Co-A6- m ($m = 0, 8, 23, 63, 79$), where n and m denote the degree of Co^{2+} exchange. The products of the oxidation process were identified as styrene epoxide (E) and benzaldehyde (B). Both the pristine forms, ETS-10 (Co-E10-0) and AM-6 (Co-A6-0), and Co^{2+} -exchanged forms displayed catalytic activities. With increasing n or m , the conversion, and hence the rate, increased. Specifically, the rates varied from 6.1 to 12.5 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with increasing n (Co-E10- n catalysts) and from 5.4 to 12.4 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with increasing m (Co-A6- m catalysts). In contrast, the E/B ratio decreased with increasing n or m . More specifically, the E/B ratio decreased from 2.1 to 0.1 with increasing n from 0 to 81 (Co-E10- n catalysts) and from 1.3 to 0.1 with increasing m from 0 to 79 (Co-A6- m catalysts). Co-E10-9 displayed the highest E yield and Co-A6-79 generated the highest B yield. The highest turnover frequency obtained was 36.3 $\text{Co}^{-1}\cdot\text{h}^{-1}$, which was the highest one obtained among those obtained for the Co^{2+} -exchanged zeolites and mesoporous silica reference materials studied in this work.

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1. Introduction

The catalytic oxidation of olefins in the presence of molecular O_2 is highly attractive from economic and environmental viewpoints. Particularly, the partial oxidation of olefins to epoxides and aldehydes is an industrially important reaction because epoxides and aldehydes are widely used as the precursors and intermediates for the syntheses of various fine chemicals and useful chemical products in the pharmaceutical, resin, and paint industries [1–4].

In principle, the direct oxidation of olefins with O_2 is highly unfavorable because the ground state of O_2 is a triplet, whereas

the ground states of olefins are singlets. Accordingly, the oxidation of olefins with O_2 has generally been performed in the co-presence of reductants such as H_2 , alcohols, and aldehydes. However, Tang et al. [5,6] first demonstrated that Co^{2+} -exchanged faujasite-type zeolites could effectively catalyze the oxidation of styrene with O_2 in the absence of reductants. Consequently, subsequent studies focused on the catalytic activities of various Co-exchanged and Co-containing microporous and mesoporous materials such as alkali and alkaline metal-modified Co-X [7], Co-Y [8], Co-SSZ-51 [9], Co-SBA-15 [10], Co-ZSM-5 [11–13], Co-SAPO-5 and Co-SAPO-34 [14], Co-MOR, Co-5A [15], and Co-coordinated

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organic-inorganic hybrid catalysts [16] toward the oxidation of olefins with O_2 or air. Among them, Co-X, Co-Y, and Co-SBA-15 [5–8,10] were effective in the epoxidation of olefins with molecular O_2 . Co-SSZ-51 was also active, but required higher O_2 pressures (> 4.14 bar) [9]. Conversely, other catalysts (Co-ZSM-5, Co-SAPO-5, Co-SAPO-34, Co-MOR, Co-5A, and Co-coordinated organic-inorganic hybrid material) required substantial amounts of initiators, such as *tert*-butyl hydroperoxide or cumyl hydroperoxide, to achieve high conversions [11–16]. Thus, the development of more active catalysts that do not require initiators in the target catalytic process is of interest.

ETS-10 is a unique titanosilicate that constitutes regularly spaced TiO_3^{2-} quantum wires with diameters (d) of ~ 0.67 nm (Fig. 1(a)). Furthermore, the structure comprises corner-sharing SiO_4 tetrahedra and TiO_6 octahedra linked via bridging oxygen atoms [17–19]. Formation of the structure can be described as an intergrowth of two hypothetical ordered Polymorph A (not shown) and Polymorph B (Figs. 1(b),(c)). Polymorph A has identical projection along the (100) and (010) directions to that of Polymorph B along the (110) and (110) directions. In Polymorph B, the TiO_3^{2-} quantum wires run along the (110) and (110) directions in the crystal (Figs. 1(b),(c)). Each TiO_3^{2-} quantum wire is surrounded by nanoporous silica (Fig. 1(d)), with a pore dimension of $8 \times 5 \text{ \AA}^2$. The pore structure of ETS-10 contains 12 rings in all three dimensions. Only a few microporous zeolites with a three-dimensional 12-ring pore system are known, and in this aspect ETS-10 has excellent diffusion characteristics. It is important to point out that the structure is inherently an intergrowth structure, consisting of randomly stacked layers. The basic unit is $Si_{40}Ti_8O_{104}^{16-}$, which is counterbalanced by 16 monovalent (Na^+ and K^+) cations. These counter cations can be exchanged with various other

monovalent, divalent, or trivalent cations through ion exchange. AM-6 is isostructural to ETS-10, featuring VO_3^{2-} quantum wires instead of TiO_3^{2-} quantum wires [20,21].

To date, only Co-exchanged aluminosilicates have been examined as olefin oxidation catalysts. Therefore, expanding this research area by examining the catalytic activities of titanosilicate (ETS-10), vanadosilicate (AM-6), and their Co-exchanged forms is of interest to explore the role of the titanate and vanadate quantum wires within the structures. Herein, we report the catalytic performances of ETS-10, AM-6, and their Co^{2+} -exchanged forms featuring varying degrees of Co^{2+} exchange toward the oxidation of styrene with O_2 to styrene epoxide (E) and benzaldehyde (B).

2. Experimental

2.1. Materials

Na_2SiO_3 (17%–19% Na_2O , and 35%–38% SiO_2 , Kanto), titanium isopropoxide (98%, Junsei), V_2O_5 (99%, Aldrich), H_2SO_4 (95%, Duksan), NaOH, (93%–100%, Samchun), KF (95%, Samchun), $Co(CH_3COO)_2 \cdot 4H_2O$ (Junsei), styrene (99%, Sigma-Aldrich), styrene oxide (97%, Aldrich), benzaldehyde (99%, Sigma-Aldrich), ethanol (95%, SK), and *N,N*-dimethylformamide (DMF, 99%, Samchun) were purchased and used without further purification.

2.2. Synthesis of ETS-10 with sizes of 200–300 nm

A Si source solution was first prepared by dissolving Na_2SiO_3 (18.4 g) in H_2O (60 g), to which NaOH aqueous solution (2.4 g NaOH and 20 g H_2O) was added with vigorous stirring, and the mixture was stirred for 2 h. For the preparation of the Ti source solution, titanium isopropoxide (5.7 g), H_2SO_4 (4.5 g), and H_2O (35 g) were mixed together and boiled at $100^\circ C$ for 90 min, and allowed to cool to room temperature. The Ti source solution was added dropwise to the Si source solution, and the mixture was stirred for 1 h. A dilute KF solution (1.2 g KF and 15 g H_2O) was added to the above mixture. The mixture was aged for 16 h at room temperature and transferred to a Teflon-lined autoclave, and heated at $200^\circ C$ for 22 h under static conditions. After cooling the autoclave to room temperature, the crystals were collected by centrifugation and washed with copious amounts of distilled deionized water.

2.3. Synthesis of AM-6 with sizes of 150–250 nm

To prepare the Si source solution, a NaOH solution (3 g NaOH and 20 g H_2O) was added to the sodium silicate solution composed of Na_2SiO_3 (12.2 g) and H_2O (50 g).

To prepare the V source solution, a required amount of H_2SO_4 (4.5 g) was added to a 50-mL round-bottom flask containing H_2O (10 g). Subsequently, V_2O_5 (1.4 g) and ethanol (4 g) were sequentially added to the flask. The heterogeneous mixture was refluxed for 25 min.

Subsequently, the greenish-yellow V source solution was added dropwise to the Si source solution. A dilute KF solution

Fig. 1. (a) Schematic illustration of the structure of ETS-10 or AM-6 imbedded with a three dimensional networks of SiO_2 channels (blue) and TiO_3^{2-} or VO_3^{2-} molecular wires (red) in case of polymorph B. (b) View along the [110] axis. (c) View along the [110] axis. (d) A single TiO_3^{2-} or VO_3^{2-} molecular wire (pink) surrounded by silica (gold) and a single TiO_3^{2-} or VO_3^{2-} molecular wire.

(2 g KF and 10 g H₂O) was added to the above mixture. After aging the mixture for 15 h at room temperature, the resulting gel was transferred to a 50-mL Teflon-lined autoclave, which was placed in a preheated oven at 220 °C for 16 h under static conditions. The precipitated crystals were collected, washed, and dried at 100 °C for 1 h.

2.4. Preparation of Co-exchanged ETS-10 with varying degrees of Co²⁺ exchange (Co-E10-*n*; *n* = 0, 9, 26, 68, 81)

Co²⁺-exchanged ETS-10 powders with varying ion exchange degrees of 0, 9%, 26%, 68%, and 81% were prepared. Pristine ETS-10 is denoted as Co-E10-0. For the preparation of Co-E10-9, Co-E10-26, and Co-E10-68, pristine ETS-10 (1 g) was mixed with Co(CH₃CO₂)₂ solution (50 mL) at varying concentrations of 4, 10, and 50 mmol/L, respectively. The ion exchange was conducted at 50 °C for 1 h. For the preparation of Co-E10-81, the ion-exchange was conducted thrice with 100 mL of 50 mmol/L Co(CH₃CO₂)₂ solution. All samples were washed with copious amounts of water and dried in an oven at 90 °C for 2 h.

2.5. Preparation of Co²⁺-exchanged AM-6 with varying degrees of Co²⁺ exchange (Co-A6-*m*; *m* = 0, 8, 23, 63, 79)

Co²⁺-exchanged AM-6 with varying ion exchange degrees of 0, 8%, 23%, 63%, and 79% were prepared. Pristine AM-6 is denoted as Co-A6-0. For the preparation of Co-A6-8, Co-A6-23, and Co-A6-63, pristine AM-6 (1 g) was mixed with Co(CH₃CO₂)₂ solution (50 mL) at varying concentrations of 4, 10, and 50 mmol/L, respectively. The ion exchange was conducted at 50 °C for 1 h. For the preparation of Co-A6-79, the ion-exchange was conducted thrice with 100 mL Co(CH₃CO₂)₂ solution (50 mmol/L). All samples were washed with copious amounts of water and dried in an oven at 90 °C for 2 h.

2.6. Characterization

Scanning electron microscopy (SEM) images were obtained using a field-emission scanning electron microscope (Hitachi S-4300) operating at an acceleration voltage of 20 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500/pc diffractometer using Cu K α (λ = 0.154056 nm) radiation operating at 40 kV and 200 mA. The diffractograms were recorded in the 2θ range of 3°–50° with a step width of 0.02° and 1°/min in continuous mode. The BET surface areas of the samples were determined using N₂ adsorption-desorption performed at –196 °C on a BELSORP-MAX analyzer. The samples were evacuated at 200 °C for 10 h prior to analysis. Raman spectra of the samples were recorded on an in-house-built set-up equipped with Ar⁺ ion laser (Spectra-Physics Stabillite 2017) as an excitation beam source, a spectrometer (Horiba Jobin-Yvon TRIAX 550), and a CCD detector (Horiba Jobin-Yvon Symphony) cooled at –196 °C. The wavelength of the excitation beam was 514.5 nm. The diffuse reflectance UV-Vis spectra of the samples were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer equipped with an integrating sphere. Bar-

ium sulfate was used as the reference. The diffuse reflectance spectra were converted using the Kubelka–Munk (K–M) function. Elemental analyses of the samples for Na⁺, K⁺, Co²⁺, Si, Ti, and V were conducted via energy-dispersive X-ray (EDX) spectroscopy analysis of the samples using an X-Max EDS-detector from Oxford instruments attached to a scanning electron microscope (JEOL-JSM-7600F).

2.7. Oxidation of styrene with molecular O₂

Co-E10-*n* and Co-A6-*m* powders were vacuum dried at 150 °C for 10 h. The dehydrated powders were transferred to a glove box charged with high-purity Ar. To examine the catalytic activity of the powders, each dehydrated powder sample (100 mg) was transferred to a round-bottom flask. The reactions were carried out in a 25-mL round-bottom flask equipped with a water-cooled condenser and an oxygen inlet to introduce oxygen. The reaction mixture was continuously stirred using a magnetic stirrer. The temperature of the reactor was maintained at 95 °C. In a typical reaction, the dehydrated catalyst powder (100 mg, 0.22 mmol) was first dispersed in DMF (20 mL) by sonication. Subsequently, styrene (500 mg, 5 mmol) was introduced into the reaction system. The reaction was carried out at 95 °C with continuous bubbling of O₂ (4 mL/min) into the reactor. After 4 h of reaction, the catalyst was removed from the reaction mixture by centrifugation and the products in the supernatant solution were analyzed by gas chromatography mass spectrometry. A reaction temperature of 95 °C and a reaction time of 4 h were chosen because conversion saturation could be obtained under these reaction conditions. The conversion is based on the amount of styrene consumed in the reaction mixture.

3. Results and discussion

3.1. XRD analysis

The crystallinity of the Co-E10-*n* and Co-A6-*m* powders was analyzed by XRD, and the patterns are shown in Fig. 2. All samples displayed characteristic diffraction patterns of ETS-10-type phase. In general, the Co²⁺ ion exchange did not affect the crystallinity of the catalysts except for the gradual slight decreases in the intensity of the diffraction peaks at 2θ = 12.16° and 28.34° and slight increases in the intensity of the peaks at 2θ = 12.96°, 17.88°, and 20.06° with increasing degrees of ion exchange. Importantly, the Co²⁺ ion exchange did not induce any collapse of the Co-E10-*n* and Co-A6-*m* structures.

3.2. SEM studies

The SEM images of the Co-E10-*n* and Co-A6-*m* samples are shown in Fig. 3. As observed, the crystals adopted a truncated tetragonal bipyramidal structure and were rather uniform in size. The surfaces were very smooth, and secondary phases or unreacted gel were absent in the samples. The lengths, *L*, in the (110) and (001) directions were 200–300 nm for Co-E10-*n* and

Fig. 2. XRD patterns of Co-E10-*n* (a) and Co-A6-*m* (b). Pristine ETS-10 and AM-6 denoted as Co-E10-0 and Co-A6-0, respectively.

150–250 nm for Co-A6-*m*.

3.3. N_2 adsorption-desorption analysis

The pore structures of the Co-E10-*n* and Co-A6-*m* samples were studied by N_2 sorption. The N_2 sorption isotherms of the samples were measured within a relative pressure (p/p_0) range of 10^{-6} to 0.998; the isotherms are shown in Fig. 4. As observed, all samples displayed Type I isotherms according to the classification of BET, which is typical of microporous materials. The BET surface areas of the Co-E10-*n* samples ($n = 0, 9, 26, 68, 81$) were respectively 412, 410, 391, 358, and 337 m^2/g and those of the Co-A6-*m* samples ($m = 0, 8, 23, 63, \text{ and } 79$) were respec-

Fig. 4. N_2 adsorption-desorption isotherms of Co-E10-*n* (a) and Co-A6-*m* (b).

tively 397, 386, 373, 349, and 333 m^2/g . Thus, as deduced, as the degree of Co^{2+} -ion exchange increased, the surface area gradually decreased. This trend indicated the onset of a slight structure collapse as the degree of Co^{2+} ion exchange increased, though the samples featured comparable XRD patterns and SEM results with no noticeable differences regardless of the ion exchange degree. Additionally, Co-A6-0 (pristine AM-6) displayed a similar surface area to that of previously reported high-quality AM-6 [21,22], thereby indicating that the crystallinity of Co-A6-0 is very high. The relative crystallinity, BET surface areas, and other structural information of the Co-E10-*n* and Co-A6-*m* samples are summarized in Table 1.

Fig. 3. SEM images of Co-E10-*n* with $n = 0$, pristine ETS-10 (a), 9 (b), 26 (c), 68 (d), and 81 (e) and of Co-A6-*m* with $m = 0$, pristine AM-6 (f), 8 (g), 23 (h), 63 (i), and 79 (j). Scale bar = 300 nm.

Table 1

Chemical compositions and physical properties of catalysts used in this study.

Catalyst	Composition	Degree of Co ²⁺ exchange (%)	Weight % of Co ²⁺	Crystallinity (%)	Surface area (m ² /g)	Raman band width (cm ⁻¹)
Co-E10-0	Na _{1.6} K _{0.40} TiSi ₅ O ₁₃	0	0.0	100	412	29
Co-E10-9	Co _{0.09} Na _{1.43} K _{0.40} TiSi ₅ O ₁₃	9	1.1	96	410	30
Co-E10-26	Co _{0.26} Na _{1.10} K _{0.38} TiSi ₅ O ₁₃	26	3.4	92	391	31
Co-E10-68	Co _{0.68} Na _{0.35} K _{0.29} TiSi ₅ O ₁₃	68	8.8	87	358	43
Co-E10-81	Co _{0.81} Na _{0.17} K _{0.21} TiSi ₅ O ₁₃	81	10.5	83	337	50
Co-A6-0	Na _{1.6} K _{0.40} VSi ₅ O ₁₃	0	0.0	100	397	10
Co-A6-8	Co _{0.08} Na _{1.45} K _{0.39} VSi ₅ O ₁₃	8	1.0	94	386	11
Co-A6-23	Co _{0.23} Na _{1.21} K _{0.33} VSi ₅ O ₁₃	23	3.0	90	373	14
Co-A6-63	Co _{0.63} Na _{0.43} K _{0.31} VSi ₅ O ₁₃	63	8.1	89	349	27
Co-A6-79	Co _{0.79} Na _{0.18} K _{0.24} VSi ₅ O ₁₃	79	10.2	81	333	38

Pristine ETS-10 and AM-6 denoted as Co-E10-0 and Co-A6-0, respectively.

3.4. Raman spectroscopy analysis

The Raman spectra of the Co-E10-*n* and Co-A6-*m* samples are shown in Fig. 5. The Raman spectra of the longitudinal (along the wire) vibration modes of the –Ti–O–Ti– and –V–O–V– chains provide highly useful information on the quality and local environment of the TiO₃²⁻ and VO₃²⁻ quantum wires in Co-E10-*n* and Co-A6-*m*, respectively. The $\nu_{\max}$ value is related to the length of the quantum wires, and decreased as the length increased [22]. The high-quality ETS-10 crystals displayed $\nu_{\max}$ in the 721–724 cm⁻¹ region [23,24]. The intensity of the longitudinal vibration is related to the number of quantum wires and increased as the number increased. The

bandwidth (*fwhm*) is related to the homogeneity of the length of the quantum wires (*l*) and decreased as the homogeneity of *l* increased. Reported values of the bandwidth have been observed between 23 and 120 cm⁻¹.

The obtained $\nu_{\max}$ value at 724 cm⁻¹ for Co-E10-*n* (*n* = 0, 9, 26, 68) indicated that the average length of the titanate quantum wires in the Co-E10-*n* crystals remained unchanged regardless of the Co²⁺ exchange degree up to 68%. In contrast, Co-E10-81 displayed a shift in $\nu_{\max}$ to a lower wavenumber region, indicating that the average length of the titanate quantum wires in Co-E10-81 was shorter than that in Co-E10-*n* (*n* = 0, 9, 26, 68). The bandwidths of Co-E10-*n* (*n* = 0, 9, 26, 68, 81) were 29, 30, 31, 43, and 50 cm⁻¹, respectively. This finding indicates that though the length homogeneity of the titanate quantum wires in pristine ETS-10 (Co-E10-0) was high, it gradually decreased with increasing degrees in Co²⁺ ion exchange. Thus, the introduction of Co²⁺ led to disconnection of the titanate quantum wires.

The high-quality AM-6 displayed a Raman shift, corresponding to the longitudinal vibration of the vanadate quantum wires, at 870 cm⁻¹ with a bandwidth of 10 cm⁻¹ [20,21]. The $\nu_{\max}$ and *fwhm* of Co-A6-0 (pristine AM-6) were 867 and 10 cm⁻¹, respectively, which was indicative of the very high crystallinity of Co-A6-0. The $\nu_{\max}$ value of Co-A6-*n* (*n* = 8, 23, 63) was also 870 nm. This finding indicated that the average length of the vanadate quantum wires remained unchanged regardless of the degree of Co²⁺ exchange up to 63%. In contrast, Co-A6-79 displayed a $\nu_{\max}$ shift to a lower wavenumber region, thereby indicating that the average length of the vanadate quantum wires in this sample was shorter than that in Co-A6-*n* (*n* = 0, 8, 23, 63). The bandwidths of Co-A6-*n* (*n* = 0, 8, 23, 63, 79) were 10, 11, 14, 27, and 38 cm⁻¹, respectively. This finding indicated that though the length homogeneity of the vanadate quantum wires in pristine AM-6 (Co-A6-0) was high, it gradually decreased with increasing degrees of Co²⁺ ion exchange. Likewise, the introduction of Co²⁺ led to disconnection of the vanadate quantum wires.

3.5. UV-visible spectroscopy analysis

Pristine ETS-10 (Co-E10-0) was colorless unlike the corre-

Fig. 5. Raman spectra of Co-E10-*n* (a) and Co-A6-*m* (b).

Fig. 6. Diffuse reflectance UV-Vis spectra of Co-E10-*n* in the spectral regions of 200–800 (a), 200–400 (b), and 300–800 nm (c) and Co-A6-*m* in the spectral regions of 200–1500 (d), 200–400 (e), and 300–800 nm (f), respectively.

sponding Co²⁺-exchanged samples (*n* = 9, 26, 68, 81) that were light pink. The UV-visible spectra of the Co-E10-*n* samples are shown in Figs. 6(a)–(c) in the spectral regions of 200–800, 200–400, and 300–800 nm. The UV-visible spectrum of Co-E10-0 displayed absorption bands below 340 nm, and these of Co-E10-*n* (*n* = 9, 26, 68, 81) displayed additional bands at ~350 and ~520 nm. These new bands were obtained owing to the incorporated Co²⁺ ions. The intensity of the bands increased with increasing degrees of Co²⁺ exchange. Regarding the visible band, the absorption band blue shifted with increasing degrees of Co²⁺ exchange, indicating that it has the framework oxygen to Co²⁺ charge transfer nature.

Pristine AM-6 (Co-A6-0) was pale yellow, and the corresponding Co²⁺-exchanged samples (*m* = 8, 23, 63, 79) were light gray. The UV-visible spectra of the Co-A6-*m* samples are shown in Figs. 6(d)–(f) in the spectral regions of 200–1500, 200–400, and 300–800 nm. The UV-visible spectrum of pristine AM-6 (Co-A6-0) displayed absorption maximums (λ_{max}) at 238 (0.98), 260 (1), 558 (0.036), and 1113 (0.061) nm (the relative intensity of the bands are shown in parentheses). The spectra of Co-A6-*m* (*m* = 8, 23, 63, 79) displayed additional absorption bands at ~350 and ~520 nm owing to the incorporation of Co²⁺.

3.6. Catalytic activity studies

The catalytic activities of Co-E10-*n* and Co-A6-*m* were as-

sessed toward the oxidation of styrene with molecular oxygen (Fig. 7, Table 2). In both cases, styrene epoxide (E) and benzaldehyde (B) were obtained as the major products with trace amounts of phenylacetaldehyde. The overall rate of conversion was between 5.4 and 12.4 mol·g⁻¹·h⁻¹. Interestingly, even in the absence of Co²⁺, both Co-E10-0 (pristine ETS-10) and Co-A6-0 (pristine AM-6) were catalytically active toward the oxidation of styrene to E and B with molecular oxygen. This finding suggested that both Ti and V could also catalyze the reaction. However, the activity increased upon increasing addition of Co²⁺ content.

Comparison between the two sets of reaction profiles (Figs. 7(a) and (b)) revealed that the Co-E10-*n* catalysts were more active than the Co-A6-*m* catalysts. The higher catalytic activity was likely due to the slightly larger pore size of ETS-10 relative to that of AM-6. Furthermore, as observed, a Co²⁺ exchange level of 26% was required to reach 100% conversion using the ETS-10 catalyst system. Contrarily, a Co²⁺ exchange level of 63% was required to achieve 100% conversion using the AM-6 catalyst system. In both catalyst systems (Co-E10-*n* and Co-A6-*m*), the reaction rates increased, while the E/B ratio decreased sharply with increasing degrees of Co²⁺ ion exchange (Fig. 7(c)). The highest E/B ratio (2.1) was obtained using Co-E10-0 that was lower than those observed using other catalysts (SrCoX18, BaCoX19, Co-SBA-15-20-5.2, Co-Beta, and Co-SAPO-34), of which the E/B ratios were in the range of 3.3–5.7 (Table 3). Accordingly, we could deduce that the

Fig. 7. Plots of the conversion and the major products with respect to the degree of Co²⁺ ion in Co-E10-*n* (a) and Co-A6-*m* (b). Plots of the E/B ratio with respect to the degree of Co²⁺ ion in Co-E10-*n* and Co-A6-*m* (c). Comparison of the TOF (Co⁻¹·h⁻¹) of various catalysts for styrene to styrene epoxide conversion (d).

Co-E10-*n* and Co-A6-*m* catalysts were more suited for application in the selective production of B over that of E from styrene and molecular oxygen. In particular, the E/B ratio became very small (0.1) when the highly Co²⁺-exchanged ETS-10 and AM-6 (Co-E10-68, Co-E10-81, Co-A6-63, and Co-A6-79) were used as the catalysts. Nevertheless, it is interesting to note that in the case of Co-E10-9, the turnover frequency per Co atom per hour was 36.3, which was higher than those obtained from the other

catalysts studied (Table 3 and Fig. 7(d)).

The catalytic activity of ETS-10 exchanged with other transition metal ions, such as Cr³⁺, Mn²⁺, Fe³⁺, Ni²⁺, Cu²⁺, and Zn²⁺, was also examined. However, the resulting activities were considerably lower than that of the Co-E10-*n* catalysts, with Cr³⁺-ETS-10 displaying a conversion of 11% and E selectivity of 55%.

Table 2

Oxidation of styrene with air over Co-E10-*n* and Co-A6-*m* catalysts.

Catalyst	Conversion (%)	Rate (mmol·g ⁻¹ ·h ⁻¹)	Selectivity (%)		E/B	TOF (Co ⁻¹ ·h ⁻¹)	
			E	B		E	B
Blank	<2.5	—	45	65	0.69	—	—
Co-E10-0	49	6.1	68	32	2.1	—	—
Co-E10-9	93	11.6	59	41	1.4	36.3	25.2
Co-E10-26	100	12.5	24	76	0.3	5.2	16.5
Co-E10-68	99	12.4	12	88	0.1	1.0	7.3
Co-E10-81	98	12.3	9	91	0.1	0.6	6.3
Co-A6-0	43	5.4	56	44	1.3	—	—
Co-A6-8	73	9.1	29	71	0.4	15.0	36.7
Co-A6-23	87	10.9	15	85	0.2	3.2	18.2
Co-A6-63	99	12.4	9	91	0.1	0.8	8.2
Co-A6-79	99	12.4	7	93	0.1	0.5	6.7

Reaction conditions: dehydrated catalyst 100 mg, 95 °C, styrene 5 mmol, DMF 20 mL, O₂ ~4 mL/min, 4 h. Pristine ETS-10 and AM-6 denoted as Co-E10-0 and Co-A6-0, respectively.

Table 3

Catalytic performances of the catalysts extracted from the literature.

Catalyst	Conversion (%)	Rate (mmol·g ⁻¹ ·h ⁻¹)	Selectivity (%)		E/B	TOF (Co ⁻¹ ·h ⁻¹)		Ref.
			E	B		E	B	
Co ²⁺ -X (8.8 wt%)	45	5.6	65.0	35.0	1.9	4.0	0.04	[5]
SrCoX18	100	12.5	85.0	15.0	5.7	20.0	0.03	[7]
BaCoX19	100	12.5	83.0	17.0	4.9	26.0	0.04	[7]
Co-SBA-15-20-5.2	92.4	4.1	63.2	15.6	4.1	3.0	0.79	[10]
Co-Beta	35.5	2.1	72.8	21.9	3.3	15.3	3.85	[13]
Co-SAPO-34	37.8	1.9	76.7	17.5	4.4	3.6	0.81	[14]
Co-MOR	10.3	0.6	66.7	33.3	2.0	5.0	1.89	[15]

3.7. Recycling studies

In the subsequent studies, Co-E10-9 and Co-A6-79 were chosen as the model catalysts. Following catalysis, the catalysts were recovered from the corresponding reaction mixtures by centrifugation and washed sequentially with copious amounts of DMF and water. The catalysts were then dried in an oven at 90 °C for 1 h, and finally vacuum dried at 150 °C for 10 h. The dried catalysts were reused in subsequent catalysis reactions. As noted, the conversion and selectivity remained unchanged after four catalytic cycles (Fig. 8), thereby indicating that Co-E10-9 and Co-A6-79 are highly stable and can be used efficiently with no loss in catalytic activity.

3.8. Proposed reaction mechanism

Based on the current study and other literature reports [7,10], a plausible reaction mechanism for the epoxidation of styrene with molecular oxygen over Co²⁺-containing catalysts is shown in Scheme 1. It is expected that DMF molecules coordinate to the extraframework Co²⁺ cations (ZO)Co²⁺ present in the zeolite pores through the oxygen atom of DMF resulting in the formation of (DMF,ZO)Co²⁺. The Co²⁺ cation in (DMF,ZO)Co²⁺ is electron rich because it is coordinated to the negatively charged framework oxygen atoms. Consequently, (DMF,ZO)Co²⁺ attracts O₂. Subsequently, an oxygen molecule (O₂) coordinates to the Co²⁺ ion, resulting in the formation of a cobalt superoxo complex (DMF,ZO)Co³⁺-OO• (I). A styrene molecule coordinates to I through the vinyl group to form

Fig. 8. Recycle test of the catalysts in styrene conversion with molecular oxygen on Co-E10-9 (a) and Co-A6-79 (b). Reaction conditions: same as Table 2.

(DMF, ZO, Styrene)Co³⁺-OO• (II). Through migratory insertion, II rearranges to an intermediate III. Then, III disintegrates to the cyclic peroxide IV and (DMF,ZO)Co²⁺. The cyclic peroxide IV then undergoes two different types of reactions: (1) thermal decomposition to benzaldehyde and formaldehyde and (2) transfer of an oxygen atom to another styrene molecule to form two styrene epoxide molecules.

4. Conclusions

Pristine ETS-10 (Co-E10-0) and AM-6 (Co-A6-0) displayed catalytic activities toward the oxidation of styrene with molecular O₂ to styrene epoxide and benzaldehyde in DMF. The corresponding Co²⁺-exchanged powders showed higher catalytic activities, and the activity increased with increasing degrees of ion exchange. Contrary to the conversion, the E/B ratio decreased with increasing *n* or *m* reaching 0.1. Therefore, highly

Scheme 1. A possible reaction mechanism for the oxidation of styrene into epoxide and benzaldehyde with air as the oxidant. ZO denotes E10-*n* and A6-*m*.

Graphical Abstract

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Co-ETS-10 and Co-AM-6 as active catalysts for the oxidation of styrene to styrene oxide and benzaldehyde using molecular oxygen

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ETS-10, AM-6, and their corresponding Co^{2+} -exchanged forms were examined as catalysts toward the oxidation of styrene in oxygen atmosphere. The conversion increased, whereas the styrene epoxide/benzaldehyde product ratio decreased with increasing degrees of Co^{2+} exchange. In the absence of Co^{2+} , pristine ETS-10 and AM-6 were catalytically active toward the formation of styrene epoxide.

Co^{2+} -exchanged ETS-10 and AM-6 (Co-E10-68, Co-E10-81, Co-A6-63, Co-A6-79) are very good catalysts for the selective production of B from styrene and molecular O_2 . The highest turnover frequency obtained was $36.3 \text{ Co}^{-1} \cdot \text{h}^{-1}$, which was the highest value obtained among the different Co^{2+} -exchanged zeolites and mesoporous silica studied in this work.

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