

Mass balance obtained:

1. The activity was expressed by the conversion of ethylbenzene (EB), the selectivity of purpose product (styrene)/byproduct (benzene and toluene) and the yield of product are defined by

$$X_{EB} = \frac{N_{EB, in} - N_{EB, out}}{N_{EB, in}} \times 100\%$$

$$Y_{product} = \frac{N_{product}}{N_{EB, in}} \times 100\%$$

$$S_{product} = \frac{Y_{product}}{X_{EB}} \times 100\%$$

Where $N_{EB, in}$ and $N_{EB, out}$ are the molar mass of ethylbenzene in and out of the reaction system, respectively.

2. As shown in Table 1 of the main article, the conversion of toluene, the product selectivity of styrene, ethylbenzene, xylene (including p-xylene, m-xylene and o-xylene) and other aromatics (such as trimethylbenzene, methyl-ethylbenzene and so on) are defined by

$$X_{Tol} = \frac{N_{Tol, in} - N_{Tol, out}}{N_{Tol, in}} \times 100\%$$

$$S_{product} = \frac{Y_{product}}{X_{Tol}} \times 100\%$$

Where $N_{Tol, in}$ and $N_{Tol, out}$ are the molar mass of ethylbenzene in and out of the reaction system, respectively.

Tables

Table S1. The specific surface areas and volumes of the modified X zeolites

Sample	BET surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)	K _{ED} (%)
NaX	486.7	0.22	0.15	--
HX	391.5	0.13	0.17	94.13
KX	442.1	0.15	0.14	87.26
CsX	387.3	0.14	0.12	62.87

The K_{ED} was calculated according to the following formula:

$$K_{ED} (\%) = \frac{W_{Na,i} - W_{Na,t}}{W_{Na,i}} \times 100$$

Where $W_{Na,i}$ and $W_{Na,t}$ are the mass percentage of Na in the initial NaX and treated zeolite, respectively.

Experimental

1. Infrared spectroscopy of acid or base sites of X zeolites

Infrared spectroscopy with pyridine adsorption (Py-IR) was conducted with a self-supported wafer of X zeolite sample in FT-IR spectrometry, according to the following procedure: Firstly, the sample was pre-treated under vacuum at 400 °C. Secondly, pyridine adsorption was conducted at 100 °C. After carrying out outgas under high vacuum, Py-IR spectrums of the sample were obtained respectively at 200 °C and 400 °C. The characteristic peak 1540 cm⁻¹ of Py-IR spectra is assigned to Bronsted acid sites, the peak 1450 cm⁻¹ to Lewis acid sites, similar to ordinary Py-IR spectrum of zeolite [H. G. Karge, J. Weitkamp, Chem. Ing. Tech. 58 (1986) 946.]. Their peak areas corresponding to Bronsted acid sites or Lewis acid sites were

determined. Besides, Py-IR of the standard ZSM-5 sample was conducted according to the same procedure. Compared X zeolite sample with the standard sample, the number of acid sites of Brønsted acid sites to Lewis acid sites on the modified X zeolites was calculated by the corresponding calibrated peak area in the external standard method.

Table S2. Determination of the acidic sites of the modified X zeolites by IR with pyridine adsorption

Zeolites	Calibrated relative area / number of		Calibrated relative area / number of	
	Bronsted acid sites		Lewis acid sites	
	473 K	673 K	473 K	673 K
HX	5.69 / 1.82	1.09 / 0.35	2.37 / 0.64	0.37 / 0.10
HX-5%Cs ₂ O	0.97 / 0.31	0.31 / 0.10	1.25 / 0.40	0.26 / 0.07
NaX	0.25 / 0.08	0.03 / 0.01	0.41 / 0.13	0.07 / 0.02
KX	0.19 / 0.06	0.03 / 0.01	0.41 / 0.11	0.07 / 0.02
CsX	0.13 / 0.04	0.01 / 0.00	0.26 / 0.07	0.04 / 0.01

Note: For Py-IR of the standard ZSM-5 sample, the calibrated relative area of the peak 1540 cm⁻¹ is 1.00 for 0.32mmol/g Bronsted acid sites, and the calibrated relative area of the peak 1450 cm⁻¹ is 1.00 for 0.27 mmol/g Lewis acid sites.

Infrared spectroscopy with phenol adsorption was conducted with a self-supported wafer of X zeolite sample in FT-IR spectrometry, according to the above procedure (phenol replacing pyridine as an absorbent). The characteristic peak 1480 cm⁻¹ of Py-IR spectra is assigned to phenol molecules on the base sites of X zeolite.

Table S3. Determination of the base sites of the modified X zeolites by IR with phenol adsorption

Zeolites	Calibrated relative area / number of base sites /(mmol/g)	
	473 K	673 K
HX	0.28 / 0.06	0.14 / 0.03
HX-5%Cs ₂ O	0.90 / 0.19	0.24 / 0.05
NaX	2.05 / 0.43	0.43 / 0.09
KX	3.62 / 0.76	1.14 / 0.24
CsX	5.33 / 1.12	1.57 / 0.33

Note: For Py-IR of the standard KX sample, the calibrated relative area of the peak 1480 cm⁻¹ is 1.00 for 0.21mmol/g base sites.

2. The effect of reaction conditions on catalytic performance

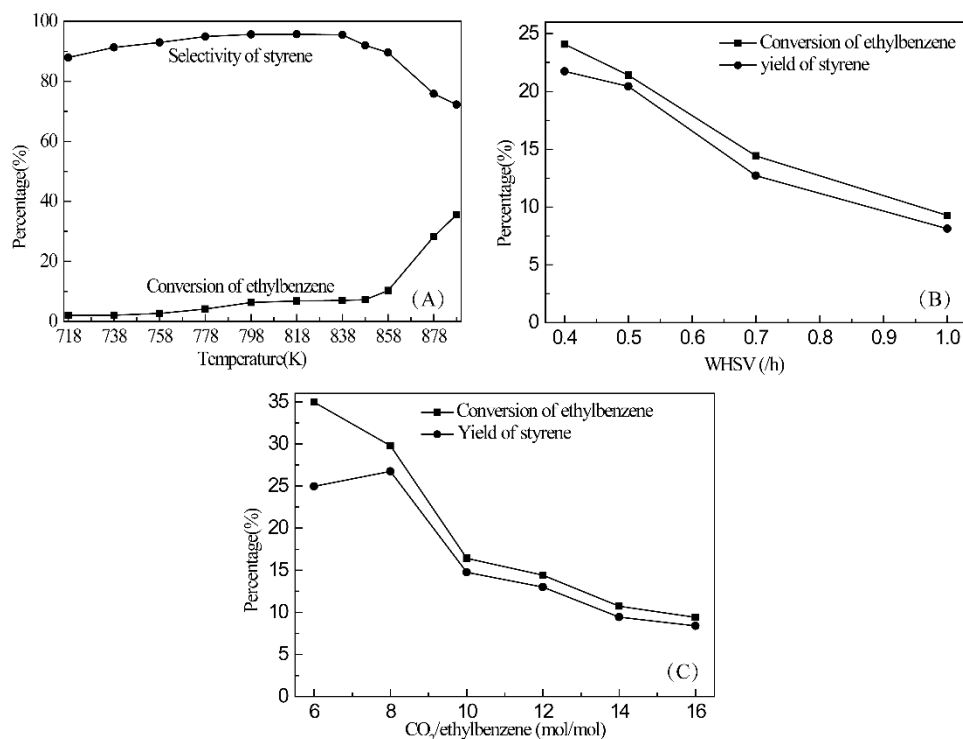


Figure S1 The effect of reaction conditions including (A) reaction temperature, reaction conditions: WHSV of 0.5 h⁻¹, atmosphere pressure, CO₂/ethylbenzene of 8.0, N₂ flow rates of 30 ml/min; (B) WHSV, reaction conditions: 858K, atmosphere pressure, CO₂/ethylbenzene of 8.0, CO₂ flow rates of 30 ml/min; (C) the molar ratio of CO₂ on ethylbenzene dehydrogenation over CsX, reaction conditions: 858K, WHSV of 0.5 h⁻¹, atmosphere pressure, CO₂ flow rates of 30 ml/min.

Figure S1 shows the activity of CsX catalyst for ethylbenzene dehydrogenation at different reaction conditions. Since this process is endothermic, CsX zeolite showed a very low catalytic activity at low temperatures, as shown in Figure S1 (A). The activity was improved only when the reaction temperature was higher than 798 K. However, when the reaction temperature reached 878 K, the side-reaction of dealkylation of ethylbenzene increased. This phenomenon can be conjectured that the α -C and β -C of ethylbenzene become more easily to be broken with a higher

temperature. In Figure S1 (B) and (C), it's observed that WHSV and the molar ratio of CO₂ to ethylbenzene significantly influenced the yield of the desired product styrene. Comparatively, the most proper WHSV is 0.5 h⁻¹ with consideration of economical values. When the molar ratio of CO₂ to ethylbenzene was lower than 8.0, the higher conversion of ethylbenzene, but lower styrene selectivity were obtained. This fact may be explained by the prolonged contact time of the reactants on the active sites over the catalyst under a lower rate of CO₂. With the increasing the molar ratio of CO₂/ethylbenzene beyond 8.0, the catalytic activity of CsX zeolite catalysts decreased.

In summary, the optimized reaction conditions for oxidative dehydrogenation of ethylbenzene with CO₂ are the reaction temperature of 818 K and WHSV of 0.5 h⁻¹ with a molar ratio of CO₂ to ethylbenzene of 8.0.

3. Catalytic activity of regenerated CsX catalyst

Table S4. Dehydrogenation of ethylbenzene with CO₂ over fresh CsX catalyst and regenerated CsX catalyst

Catalyst	Ethylbenzene conversion (%)	Styrene yield (%)	Product selectivity (%)		
			Styrene	Benzene	Toluene
Fresh	29.79	26.76	89.83	3.39	6.78
Regenerated	27.84	24.64	88.51	3.52	7.97
Second regeneration	25.60	22.10	86.34	4.03	9.63

Reaction conditions: 858K, WHSV of 0.5 h⁻¹, atmosphere pressure, CO₂/ethylbenzene of 8.0, CO₂ flow rates of 30 ml/min.