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# Acid-based co-catalysis for oxidative dehydrogenation of ethylbenzene to styrene with CO<sub>2</sub> over X zeolite modified by alkali metal cation exchange

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A variety of the modified X zeolites were used to catalyse the oxidative dehydrogenation of ethylbenzene to styrene with  $CO_2$  for the first time. The results showed that X zeolites modified by alkali metal cation exchange, such as KX and CsX, exhibited the high catalytic activity and selectivity with a good stability. The reaction temperature 818 K over the modified X zeolites is much less than 923 K over the current metallic oxide catalyst. Moreover, the cocatalysis between acid sites and base sites over the modified X zeolite was indispensable in this reaction, and the basicity of the catalyst greatly determined the selectivity of styrene. The participation of  $CO_2$  in co-catalysis process improves the conversion of ethylbenzene and the selectivity of styrene.

### **1** Introduction

As an important monomer of modern petrochemical products, styrene is widely used to produce plastics, resin copolymers and synthetic rubbers, etc<sup>1-3</sup>. Currently, 90% of styrene in the industry is produced by the catalytic dehydrogenation of ethylbenzene under a large quantity of steam. However, the reaction temperature is very high (873-973 K) and the latent heat of steam condensation cannot be recycled, these drawbacks lead to the excessive energy consumption. This process also shows the characters of the low atom economy, thermodynamic equilibrium limitations, short lifetime of catalysts, etc<sup>4, 5</sup>. Therefore, it is very crucial to develop an alternative way to produce styrene.

Driven by the increasing concern for global warming, it is urgent to reduce the emission of greenhouse gas, especially for  $CO_2$ , to meet the worldwide requirements<sup>6</sup>. One efficient way is to utilize CO<sub>2</sub> as a reactant instead of emitting it into atmosphere. Some chemical reactions can use  $CO_2$  as a source of "oxygen" atoms, or as an oxidant. For example, CO<sub>2</sub> has been found to be beneficial for oxidative dehydrogenation of ethylbenzene to form styrene, which was advocated for the first time by Sugino<sup>7</sup> in 1995. They found that the conversion of dehydrogenation of ethylbenzene over an iron-loaded activatedcarbon catalyst was highly promoted with CO<sub>2</sub>. Further research indicated that the new process using CO<sub>2</sub> as an oxidant should be an energy-saving process. The energies required for the present commercial process using steam and for the new process using CO<sub>2</sub> were estimated to be  $1.5 \times 10^9$  cal/t-styrene and  $6.3 \times 10^8$  cal/t-styrene, respectively<sup>8</sup>. Therefore, as an important economical and energy-saving process, the oxidative dehydrogenation of ethylbenzene with CO<sub>2</sub> to styrene has evoked a lot of interest<sup>9-12</sup>.

However, the dehydrogenation of ethylbenzene with CO<sub>2</sub> cannot be performed at industrial scale because of lacking of active and stable catalysts. At present, many catalysts have been prepared for the dehydrogenation of ethylbenzene with  $CO_2$  in lab. With the development of mesoporous materials, the MCM-41 or SBA-15 molecular sieves were used as promising catalyst supports for the oxidative dehydrogenation of ethylbenzene in the presence of  $CO_2^{13-19}$ . Qiao et al. loaded vanadia on mesoporous MCM-41 to promote the catalytic performance for the oxidative dehydrogenation of ethylbenzene with CO2, and they found that it was more active than vanadium supported on conventional amorphous SiO<sub>2</sub><sup>16</sup>. V, Cr, Fe or Ga/MCM-41 zeolites prepared by direct hydrothermal synthesis have been tested for dehydrogenation of ethylbenzene with CO2, and Cr-MCM-41 showed the highest catalytic activity<sup>17</sup>. CeO<sub>2</sub>-ZrO<sub>2</sub> supported on SBA-15 exhibited the superior activity than bulk single oxides for the dehydrogenation of ethylbenzene to styrene with CO<sub>2</sub> shown by Burri et al<sup>18</sup>. VOx supported on SBA-15 were also tested as a catalyst in the oxidative dehydrogenation of ethylbenzene to styrene in the presence of N<sub>2</sub>O, reported by Kus' trowski et al<sup>19</sup>. Although the high catalytic activity can be achieved over some MCM-41 or SBA-15 supported catalysts, high reaction temperature was needed above 873K, and the poor stability was not solved as well. The catalytic activity of the modified MCM-41 catalyst decreased by 30% after 6 h, and the similar phenomenon also appeared over the SBA-type catalysts. Moreover, in the above reports, few attention has been devoted to its effect of the porous structure on the dehydrogenation of ethylbenzene with  $CO_2^{13}$ , <sup>16-18</sup>. Up to now, the usual microporous zeolites have not been used to prepare the catalyst for dehydrogenation of ethylbenzene with CO<sub>2</sub>.

This work focuses on the effect of the different X zeolites on the dehydrogenation of ethylbenzene with  $CO_2$  for the first time. A variety of the modified X zeolites with different acid sites and base sites were prepared by metallic ion-exchange. After the catalytic performance of the modified X zeolites was investigated, the mechanism of acid-based co-catalysis for the dehydrogenation of ethylbenzene with  $CO_2$  was discerned.

### 2 Experimental

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### 2.1 Catalyst preparation

The Na-X zeolite (Tongxing zeolite industry, Shanghai, Si/Al=1.27) was ion-exchanged with  $NH_4^+$ ,  $K^+$ ,  $Cs^+$  to prepare NH<sub>4</sub>-type X, KX, CsX, respectively. CsOH was used as a source of Cs<sup>+</sup> according to the method reported by Wahab et al.<sup>20</sup>, NH<sub>4</sub>Cl and KHCO<sub>3</sub> were used as the sources of NH<sub>4</sub><sup>+</sup> and K<sup>+</sup>, respectively. An aqueous solution of CsOH (400 ml, 0.75 M) and NaX (20 g) were mixed, stirred for 5 min and kept for 4 h at 363 K. The slurry was filtered with Buchner funnel. The filtered cake was dried in an oven at 373 K for 12 h and calcined at 793 K for 4 h in a muffle furnace in air. The sample was again immersed in an aqueous solution of CsOH (400 ml, 0.75 M), stirred and kept for 4 h at 363 K. The above procedures were repeated for two more times (total 3 times). The obtained catalyst was pressed, crushed, and sorted to get parent CsX catalysts (particles of 12-20 mesh, denoted as CsX). KX and NH<sub>4</sub>-type X were prepared following the same method by replacing the precursor solution with 1.0 M KHCO<sub>3</sub> and 1.0 M NH<sub>4</sub>Cl, respectively. NH<sub>4</sub>-type X was calcined at 793 K for 2 h with a ramp of 3 K min<sup>-1</sup> to obtain H-type X, denoted as HX.

HX containing  $Cs_2O$  was prepared by impregnation of HX with CsOH solution, and calcined at 793 K for 2 h after drying. The modified catalyst was denoted as HX-D%Cs<sub>2</sub>O, where D referred to the weight percentage of  $Cs_2O$  in the catalyst.

### 2.2 Catalyst characterization

The X-ray diffraction patterns of catalysts were recorded on a BRUKER D8 ADVANCE diffractometer using Cu Ka radiation, which was operated at 40 kV and 40 mA. A scanning rate of 5 °/min was used for Bragg's angles  $2\theta = 5-50^\circ$ . The specific surface area of catalysts was determined by nitrogen adsorption at 77 K on a Quantachrome Nova-2200e sorptometer and calculated by the Brunauer-Emmett-Teller (BET) method. Samples were pre-treated at 573 K for 3 h in a vacuum prior to the measurement. The elemental compositions of catalysts were determined by inductively coupled plasma (ICP, OPTIMA2100DV, Perkin Elmer). The acidity of catalysts was determined by pyridine-infrared spectroscopy (Py-IR) (Bruker IFS-88). The basicity of catalysts was determined by test reaction of the alkylation of toluene with methanol and characterized by IR with phenol adsorption. The test reaction conditions were as follows: reaction temperature 703 K, Toluene/Methanol molar ratio of 5, WHSV of 1.0 h<sup>-1</sup>. with nitrogen as carrier gas at atmosphere pressure. TG curves were measured with a NETZSCH STA449C for the uncalcined samples, with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> being used as a reference sample. The sample was heated at a rate of 10 K/min in a static air.

### 2.3 Catalyst evaluation

The reaction of dehydrogenation of ethylbenzene in the presence of  $CO_2$  was carried out in a fixed bed tubular reactor

(i.d. 1.5 cm and length 50 cm) at 818 K with WHSV of 0.5 h<sup>-1</sup> under atmospheric pressure. 5.0 g catalyst particles were packed into a stainless steel and pre-treated in a flowing N<sub>2</sub> (30 ml/min) at 818 K for 2 h. Then, ethylbenzene was pumped into the reactor by a metering pump (Laballiance Series III pump) with the weight hourly space velocity (WHSV) of 0.5 h<sup>-1</sup>. The reactor effluent was analysed with online gas chromatograph HP-5890 equipped with a FID detector and a 50 m HP-FFAP capillary column in order to obtain the distribution of the products.

### **3** Results and discussion

### **3.1** Characterizations of the modified X zeolites



Figure 1 XRD patterns of different ion-exchanged X zeolites

As can be seen in Figure1, all the samples exhibit sharp XRD peaks at  $6.2^{\circ}$ ,  $10.1^{\circ}$ ,  $15.5^{\circ}$ ,  $23.4^{\circ}$ ,  $26.7^{\circ}$  and  $31.0^{\circ}$ , which are the characteristic peaks of the faujasite structure. However, the strength of characteristic diffraction peaks slightly decreased, compared to NaX. This change may be attribute to the damage of the framework of zeolites in the process of ion exchange (shown in Table S1). Besides, CsX zeolite showed the different intensity distribution. The peak at  $15.5^{\circ}$  almost disappears, and the peaks at  $25.43^{\circ}$  and  $29.20^{\circ}$  significantly increase. It attributes to the incorporation of Cs cations, which have different scattering properties. In addition, neither obvious shift in the peak positions nor significant diffraction lines assigned to any new phase were observed in the XRD patterns of the modified samples. Above these facts indicate that the crystal structure of X zeolite is remained after ion exchange.

The characterization of surface properties of materials as acid catalysts or base catalysts is necessary for predicting the catalytic performance. For X zeolites, several methods were reported<sup>21</sup>, such as indicator/titration methods<sup>22, 23</sup>, use of probe molecules<sup>24, 25</sup>, calorimetry and temperature programmed desorption, spectroscopy of adsorbed molecules<sup>26-30</sup>, and testing reactions<sup>31-34</sup>, etc. Generally, the base catalysts lead to side-chain alkylation in aromatic alkylation, while the acid catalysts bring about ring alkylation. For example, the reaction of toluene with methanol over basic zeolites produces styrene and ethylbenzene, while xylene was formed over acid zeolites<sup>31, 35</sup>. Therefore, these two catalytic reactions could be used for identifying the surface acidity or basicity of the modified X zeolites in this work. The results are shown in Table 1.

As listed in Table 1, different modified X-type zeolites exhibited different reactivity in the alkylation of toluene with

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methanol. KX and CsX presents 3.91% and 7.10% conversion of side-chain alkylation of toluene with methanol, only producing ethylbenzene and styrene. HX and HX-5%Cs<sub>2</sub>O zeolite catalysts led to aromatic-ring alkylation (9.25% and 3.91% conversion of toluene), with xylene as the main product. NaX zeolite catalysed the side-chain alkylation and aromaticring alkylation simultaneously, with the reaction products of styrene (6.50%), ethylbenzene (13.52%), xylenes (55.83%) and other aromatics (24.15%). Above these facts imply that alkali cation-exchanged zeolites such as KX and CsX mainly possess base sites, and NaX zeolite possesses both weaker base sites and acid sites. In contrast, there are mainly acid sites on HX and HX-5%Cs<sub>2</sub>O zeolites. Different types of alkali metal ionexchanged X zeolites were applied to the side chain alkylation of toluene with methanol by Yashima<sup>31</sup>. They found that total basicity of molecular sieve was proportional to the catalytic activity of side-chain alkylation of toluene with methanol, and the catalytic activity of CsX was higher than KX. Other investigations on the side-chain alkylation of toluene with methanol by adjusting the acid-based property of X zeolite drew the same conclusion<sup>36-39</sup>. From Table 1, X zeolites modified by K<sup>+</sup>, Cs<sup>+</sup> showed higher catalytic activity for the side-chain alkylation, whereas HX zeolite showed higher catalytic activity for the aromatic-ring alkylation. This phenomenon arises from the order of total alkalinity of X-type zeolites, ranking as HX < NaX < KX < CsX.

Table 1. Different X-type zeolites for the alkylation of toluene with methanol

	Toluene	Product selectivity (%)			
Catalyst	conversion (%)	Styrene	Ethylbenzene	electivity (%) ne Xylene 55.83 87.92 82.36	Other aromatics
NaX	1.21	6.50	13.52	55.83	24.15
HX	9.25	0	0.72	87.92	12.08
НХ- 5%Сs <sub>2</sub> О	6.16	0	0	82.36	16.92
KX	3.91	20.62	79.38	0	0
CsX	7.10	20.70	79.30	0	0

Reaction conditions: 703 K, Toluene/Methanol molar ratio of 5.0,

WHSV of  $1.0 h^{-1}$ , atmosphere pressure (N<sub>2</sub>), N<sub>2</sub> flow rate of 30 ml/min. The detailed calculation equation of the conversion, selectivity and yield is shown in the supplementary material (with page 1, Mass balance obtained, 2).

The amount of acid sites and base sites of the modified X zeolites were also characterized by IR with pyridine adsorption and phenol adsorption, as shown in Table 2 & Table 3, respectively. More detailed dates are shown in Table S2 and Table S3. Obviously, the total acidity of X-type zeolites was in order of HX > HX-5%Cs<sub>2</sub>O > NaX > KX > CsX, whereas the total basicity behaved a completely opposite tendency. The loading of Cs<sub>2</sub>O or ion exchange with K<sup>+</sup>, Cs<sup>+</sup> increased the total basicity of X zeolite, which significantly accompanied with the reduction of acidity. The characterization results are in accordance with the results obtained from the reaction of the alkylation of toluene with methanol.

Table 2. Determination of the acid sites of the modified X zeolites by IR with pyridine adsorption

Zaalitaa -	Bronsted acid (mmol/g)		Lewis acid (mmol/g)		
Zeontes	473 K	673 K	473 K	673 K	
HX	1.82	0.35	0.64	0.10	
HX- 5%Cs <sub>2</sub> O	0.31	010	0.40	0.07	
NaX	0.08	0.01	0.13	0.02	
KX	0.06	0.01	0.11	0.02	

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Zaalitaa	Base sites /(mmol/g)			
Zeontes	473 K	673 K		
HX	0.06	0.03		
HX-5%Cs <sub>2</sub> O	0.19	0.05		
NaX	0.43	0.09		
KX	0.76	0.24		
CsX	1.12	0.33		

3.2 Catalytic performance of the modified X zeolites for the oxidative dehydrogenation of ethylbenzene with  $CO_2$ 



Figure 2 The selectivity of oxidative dehydrogenation of ethylbenzene with  $CO_2$  over the modified X zeolites

Reaction conditions: 818K, WHSV of 0.5 h<sup>-1</sup>, atmosphere pressure, CO<sub>2</sub>/ethylbenzene of 8.0, CO<sub>2</sub> flow rates of 30 ml/min, obtained from Figure S1.

Four X-type zeolites were applied to catalyze the oxidative hydrogenation of ethylbenzene with  $CO_2$ . Comparatively, KX and CsX exhibited high selectivity for styrene, as shown in Figure 2. The selectivity of styrene over NaX firstly increased, then decreased, and the selectivity of styrene over HX zeolite were increasing with time on stream. The specific catalytic performance of all catalysts is shown in Figure 3 and Table 4.



Figure 3 The oxidative dehydrogenation of ethylbenzene with  $\mathrm{CO}_2$  over HX zeolite

Reaction conditions: 818K, WHSV of 0.5  $h^{-1}$ , atmosphere pressure, CO<sub>2</sub>/ethylbenzene of 8.0, CO<sub>2</sub> flow rates of 30 ml/min, obtained from Figure S1.

As shown in Figure 3, with increasing the reaction time, the conversion of ethylbenzene, the selectivity of styrene and other by-products show different trends over HX. Combining with Table 4, it can be seen that HX, NaX, KX and CsX behaved different catalytic properties for ethylbenzene dehydrogenation, forming the different products including styrene, benzene and toluene. Besides, CO and H<sub>2</sub> were detected in the effluent gases, but the content of H<sub>2</sub> was very low. It is suggested that  $CO_2$  behaves as an oxidant for the oxidative dehydrogenation of ethylbenzene to styrene.

 
 Table 4 Dehydrogenation of ethylbenzene with CO2 over different Xtype zeolites

Catalyst	Ethylbenzene conversion (%)	Styrene yield (%)	Product selectivity (%)		
			Styrene	Benzene	Toluene
NaX	9.47	8.49	89.61	3.02	7.37
KX	10.53	9.69	92.08	2.27	5.56
CsX	6.94	6.65	95.41	0	4.59
НХ- 5%Сs <sub>2</sub> О	2.57	1.87	72.59	8.87	18.96

Reaction conditions: 818K, WHSV of 0.5 h<sup>-1</sup>, atmosphere pressure,  $CO_2$ /ethylbenzene of 8.0,  $CO_2$  flow rates of 30 ml/min, obtained from Figure S1.

The detailed calculation equation of the conversion, selectivity and yield is shown in the supplementary material (with page 1, Mass balance obtained, 1).

At the initial reaction stage, HX catalyst has higher activity, and the conversion of ethylbenzene can be up to 18.70%. However, ethylbenzene was mainly converted to benzene (50.37%) and toluene (22.14%) by dealkylation. The selectivity of objective styrene was only 18.98%, accompanied by a small amount of xylenes. As the reaction proceeds, the conversion of ethylbenzene was gradually reduced. However, the selectivity of styrene was increasing. As can be seen from Table 4, the reaction of ethylbenzene dehydrogenation has much higher selectivity over NaX (89.61%), KX (92.08%) and CsX (95.41%) than HX (16.14%) or HX-5%Cs<sub>2</sub>O (72.59%). Among them, KX catalyst shows the highest activity, and there is no benzene formed over CsX zeolite. In conclusion, it shows the distinct catalytic properties over different modified X zeolites for the oxidative dehydrogenation of ethylbenzene with CO<sub>2</sub>.

There are a lot of acid sites on the fresh HX zeolite, which are the active sites for the dealkylation and disproportionation of ethylbenzene. Therefore, the conversion of ethylbenzene is high and the selectivity of styrene is low at the initial stage. Generally, the strong acid sites on the surface of zeolites can cause the by-reaction to generate coke deposition, and the coke deposition in turn covers these strong acid sites. Therefore, the reactivity of dealkylation and disproportionation reaction significantly decreased after 4h with the decreasing of the selectivity of benzene (from 56.02% to 14.90%) and toluene (from 20.87% to 12.96%). As a result, the selectivity of styrene significantly increased from 16.14% to 72.14% without forming multi-methylbenzene. In addition, the introduction of Cs<sub>2</sub>O species to HX zeolite, which neutralized a part of strong acid sites, weakens the activity of ethylbenzene dealkylation significantly (Table 4). This result indicates that the strong acid sites tend to cause side reactions, such as ethylbenzene dealkylation and disproportionation, etc.

As can be seen in Table 4, the catalytic activity of KX, NaX and CsX zeolite for the oxidative dehydrogenation of ethylbenzene with  $CO_2$  follows the order of KX > NaX > CsX.

This phenomenon indicates that the basic strength of catalysts is too high to be unfavourable for this catalytic process.

Cesium oxide has been loaded onto HX zeolite to adjust the surface acidity and basicity by covering some acid sites and introducing the proper base sites. This modification greatly improved the selectivity of styrene (from 16.14% to 72.59). However, the reactivity remarkably decreased (from 56.02% to 2.57%) with the reduction of acid sites.

Based on the above results, it is considered that the co-catalysis between acid sites with base sites is indispensable for the oxidative dehydrogenation of ethylbenzene to styrene with  $CO_2$ , and the basic strength of the catalyst greatly influences the selectivity of styrene.

# 3.3 The mechanism of oxidative dehydrogenation of ethylbenzene with $\mathrm{CO}_2$ over $\mathrm{CsX}$

Compared to other modified X zeolites, CsX showed the highest selectivity of styrene product. Figure 4 shows ethylbenzene conversion over CsX under different carrier gas conditions. Under the condition of 818 K without carrier gas, ethylbenzene dealkylation and other side-reactions happened over CsX catalyst, and ethylbenzene mainly converted to the side products of benzene and toluene. Sakurai et al.40 considered that the contact time was prolonged in the absence of any carrier gas, and the conversion of ethylbenzene increased with increasing side reactions, such as the thermal cracking of ethylbenzene and styrene. When N<sub>2</sub> was used as carrier gas, the contact time of reactants over X zeolite became less, thus the incidence of reactions reduced. Moreover, the conversion of ethylbenzene was less than 2% in this case, with the main reaction product of toluene. However, when the carrier gas was CO<sub>2</sub>, the conversion of ethylbenzene and the selectivity of styrene significantly increased, reaching 29.79% and 89.83%, respectively (the experimental data including the more detailed discussion shown in the section (Figure S1) of the electronic supplementary information about the effect of reaction conditions). Therefore, an appropriate flow rate of CO<sub>2</sub> can adjust the reaction contact time, and facilitate the diffusion of reactants and desorption of reaction products to reduce the occurrence of side reactions. On the other hand, CO<sub>2</sub> can participate in co-catalysis process, promoting ethylbenzene dehydrogenation as well as enhancing the conversion of ethylbenzene and the selectivity of styrene.



Figure 4 Ethylbenzene conversion over CsX under different carrier gases

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Reaction conditions: 818 K, WHSV of 0.5 h<sup>-1</sup>, atmosphere pressure, CO<sub>2</sub>/ethylbenzene of 8.0, N<sub>2</sub>/ethylbenzene of 8.0, N<sub>2</sub>/CO<sub>2</sub> flow rates of 30 ml/min, obtained from Figure S1.

In addition, in comparison to the selectivity of styrene and the by-products over all X-type zeolites (HX, HX-5%Cs<sub>2</sub>O, NaX, KX, CsX), it's found that the coordination between proper base sites and acid sites is more beneficial for the dehydrogenation of ethylbenzene to styrene. This result is similar to the conclusion the combination of ethvlbenzene on dehydrogenation and CO<sub>2</sub> shift-reaction over a sodium oxide/alumina catalyst by Sato et al<sup>41</sup>. Based on the above facts, the mechanism of oxidative dehydrogenation of ethylbenzene with CO<sub>2</sub> over the modified X zeolites was suggested, as shown in the Figure 5.



Figure 5 Schematic of oxidation dehydrogenation of ethylbenzene with  $CO_2$  over the modified X zeolites

Firstly, ethylbenzene is strongly adsorbed on the large cations of zeolite extra framework due to the interactions of the ethylbenzene  $\pi$ -electrons (electron pair donor) and the cation (electron pair acceptor). These interactions withdraw electron from the aromatic ring and facilitate the polarization of the  $\alpha$ -H of ethyl. Additionally, the ethyl group of ethylbenzene interacts with the oxygen atoms of the basic framework, further polarizing the  $\alpha$ -H of ethyl<sup>42</sup>. Secondly, a negatively charged O<sup>-</sup> is formed from CO<sub>2</sub> adsorbed on the other oxygen atoms of the basic framework with a C-atom polarized positively. The negatively charged O<sup>-</sup> is bonded with the positively charged  $\alpha$ -H, simultaneously polarized and captured a  $\beta$ -H. Finally, styrene molecules desorb from the X zeolites, and CO<sub>2</sub> molecules activated by base sites react with the protons to produce H<sub>2</sub>O and CO. In this way, the process of the oxidative dehydrogenation of ethylbenzene is completed. Therefore, the cooperation of acid sites and base sites over the modified X zeolites promotes the oxidative dehydrogenation of ethylbenzene with CO2 efficiently.

### 3.4 Catalytic stability with time on stream

As CsX showed the highest styrene selectivity, the catalytic stability for the oxidative dehydrogenation of ethylbenzene with  $CO_2$  was tested over CsX zeolite under the optimized condition.



**Figure 6** The stability of CsX catalyst: (A) catalytic performance with time on stream; (B) TG of the used CsX zeolite Reaction conditions:858K, WHSV of  $0.5 \text{ h}^{-1}$ , atmosphere pressure, CO<sub>2</sub>/ethylbenzene of 8.0, CO<sub>2</sub> flow rates of 30 ml/min;

As shown in Figure 6, CsX zeolite catalyst presents a 29.94% conversion of ethylbenzene with high styrene selectivity good stability (46h) for (89.59%)and oxidative dehydrogenation of ethylbenzene with CO<sub>2</sub>. At the initial stage of the reaction, the catalytic activity of CsX gradually increased from 16.10% to 29.94%. It indicates that the catalyst need to be activated, then it exhibits a higher catalytic activity. During the initial 39 h, the selectivity to styrene was stable (around 90%). Then the styrene selectivity gradually decreased from 89.59% to 69.75% with increasing activity of ethylbenzene dealkylation to toluene and benzene. The catalysts became deep black after time on stream of 46 h. The TG curve of the used CsX has two obvious weight loss peaks located at 333  $\sim$  553 K and 673  $\sim$ 1043 K, respectively. The first weightlessness peak should be attributed to the peak of desorption of volatile organic compounds or decomposition components, and the second weight loss peak is assigned to the decomposition of coke. The amount of coke over CsX is 9.91% after 46 h. As shown in Table S4, after the used zeolite was calcined at 873 K for 6 h in air atmosphere, the catalytic activity and the selectivity of styrene could be recovered to the level of fresh catalyst. And after the second time regeneration, the activity of catalysts can return to about 86% of the fresh catalyst with a little reduction. Therefore, it can be confirmed that coke deposition on CsX zeolite is the main reason for the catalyst deactivation in the oxidative dehydrogenation of ethylbenzene with CO<sub>2</sub>.

### Conclusions

Oxidative dehydrogenation of ethylbenzene to styrene with CO<sub>2</sub> was investigated over X-type zeolites modified by cation exchange. Alkali-metal-modified X zeolites such as KX and CsX show high catalytic activity and selectivity with a good stability for ethylbenzene dehydrogenation to styrene with CO<sub>2</sub>. In comparison to the catalytic performance of the modified X zeolites with the different strength of acid sites and base sites, it is found that the coordination of proper base sites and acid sites is indispensable for oxidative dehydrogenation of ethylbenzene to styrene with  $CO_2$ . In addition, the appropriate basic strength of the catalyst directly determines the high selectivity of the objective product (styrene) with little formation of by-products. These results further validate the catalytic mechanism of acidbased coordination over the modified X zeolites. The effective co-catalysis can be reached by optimizing the acid-based sites and the microporous structure of the modified X zeolites to further enhance its catalytic performance for oxidative

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