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Role Of CO₂ As a Soft Oxidant For Dehydrogenation of Ethylbenzene to Styrene over a High-Surface-Area Ceria Catalyst

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ABSTRACT: Catalytic performance and the nature of surface adsorbates were investigated for high-surface-area ceria during the ethylbenzene oxidative dehydrogenation (ODH) reaction using CO₂ as a soft oxidant. The high surface area ceria material was synthesized using a template-assisted method. The interactions among ethylbenzene, styrene, and CO₂ on the surface of ceria and the role of CO₂ for the ethylbenzene ODH reaction have been investigated in detail by using activity test, in situ diffuse reflectance infrared and Raman spectroscopy. CO₂ as an oxidant not only favored the higher yield of styrene but also inhibited the deposition of coke during the ethylbenzene ODH reaction. Ethylbenzene ODH reaction over ceria followed a two-step pathway: ethylbenzene is first dehydrogenated to styrene with H₂ formed simultaneously, and then CO₂ reacts with H₂ via the reverse water gas shift. The produced styrene can easily undergo polymerization to form polystyrene, which is a key intermediate for coke formation. In the absence of CO₂, the produced polystyrene transforms into graphite-like coke at temperatures above 500 °C, which leads to catalyst deactivation. In the presence of CO₂, the coke deposition can be effectively removed via oxidation with CO₂.

KEYWORDS: high-surface-area ceria, oxidative dehydrogenation, ethylbenzene, styrene, CO₂, infrared spectroscopy, Raman spectroscopy, coking

INTRODUCTION

Styrene is one of the most important chemicals in the petrochemical industry for the production of polymers, including polystyrene and styrene–butadiene rubber. Styrene has been mainly produced by ethylbenzene dehydrogenation in the presence of an iron oxide catalyst with excess supply of steam at high temperature (600–650 °C). Typical catalysts used in the dehydrogenation of ethylbenzene are K–Fe₂O₃ catalysts; however, there are a few problems associated with the dehydrogenation of ethylbenzene, such as the large amount of energy consumption during the process, the low yield of styrene due to thermodynamic limitation of endothermic reaction, irreversible catalyst deactivation, and deposition of dehydrogenated carbonaceous species (i.e., coke). Therefore, an economic and efficient ethylbenzene dehydrogenation process is in high demand. Various methods have been attempted to solve the above-mentioned problems of using steam during the dehydrogenation of ethylbenzene. The oxidative dehydrogenation (ODH) process of ethylbenzene to styrene in the presence of oxidant has attracted considerable attention because it can be operated at lower temperatures and ethylbenzene conversion would not be equilibrium limited. A variety of oxidizing agents, such as O₂, N₂O, SO₂ and CO₂, have been used for the oxidative dehydrogenation of ethylbenzene to lower the reaction temperature. Exploitation of CO₂ as a soft oxidant for the commercial catalytic ODH of ethylbenzene to styrene has received enormous interest recently because of several benefits of using CO₂ compared with other oxidants. It has been reported that CO₂ can act as a soft oxidant as well as diluent. In addition, CO₂ stays in the gas form throughout the reaction and so does not need latent heat for vaporization. CO₂ can also decrease the partial pressure of reactants more effectively than steam, and it has the highest heat capacity among various gases. In addition, in the presence of CO₂, coupling between reverse water–gas shift reaction

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO} \]  

(1)

and the ethylbenzene dehydrogenation becomes more favorable. However, it has been reported that a small...
amount of CO₂ inhibits the catalytic activity of ethylbenzene dehydrogenation as a result of the decomposition of the active phase of iron oxide catalyst in the presence of CO₂. Thus, using CO₂ was largely limited in the process for preparing styrene because of its property of deactivating the ferrite compounds. It is necessary to develop a catalyst to retain sufficient activity and selectivity when using CO₂ for the styrene production process.

Good performance for dehydrogenation of ethylbenzene has been reported for a solid catalyst containing vanadium as an active component, wherein CO₂ serves as oxidant and without steam. Others also reported that the enhancement effects of the dehydrogenation activity of ethylbenzene were significant with CO₂ in the presence of Fe₂O₃/Al₂O₃, MnO₂, ZrO₂, and a SBA-15-supported CeO₂–ZrO₂ catalyst. However, the reaction temperature of dehydrogenation over these catalysts is still high (above 500 °C). Therefore, developing an efficient catalyst with high activity at lower temperature is still highly desirable.

Ceria is a key component in the formulation of many industrially important catalysts and currently attracts attention in the application of the ODH of ethylbenzene catalysts as a result of its oxygen storage/release capacities. It has been reported that ceria itself could be a good catalyst for ODH of ethylbenzene to styrene by using O₂ that helps decrease coking during the ODH reaction. However, there is safety concern using O₂, and the styrene selectivity among the products might be low due to over oxidation by O₂. CO₂ as a soft oxidant might favor the styrene yield over ceria catalyst, and it is much safer than O₂. So far, the effect of CO₂ in the reaction of the ethylbenzene ODH over the pure ceria catalyst has not been established. In this study, a high-surface-area ceria material was synthesized and tested for ethylbenzene ODH to styrene using CO₂. The role of CO₂ for the catalytic performance and coking mechanism has been investigated in detail. We find that the high-surface-area ceria prepared by the template-assisted synthesis method exhibits higher ethylbenzene conversion and styrene yield at low temperatures (400–500 °C) than commercial ceria nanoparticles. CO₂ favors ODH reaction through a two-step pathway. Ethylbenzene is first dehydrogenated to styrene, and then CO₂ reacts with the H₂ byproduct via the reverse water–gas shift. In situ DRIFTS and Raman characterization proves that CO₂ acts as a soft oxidant not only favoring the low temperature ODH of ethylbenzene over the ceria catalyst, but also inhibiting the coke deposition during the reaction.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. High-surface-area (HSA-) CeO₂ was synthesized by a template-assisted synthesis method using a non-ionic block copolymer template (Pluronic P104) as described elsewhere. Typically, Ce(NO₃)₂·6H₂O (4.4 g, 10 mmol) and Pluronic P104 (5 g) were dissolved in ethanol. The solution was stirred for 2 h and then cast into a Petri dish. The dish was placed into a preheated oven at 65 °C for 24 h and then placed into an oven at 150 °C for an additional 24 h. The sample was then calcined in air at 450 °C for 4 h. A reference commercially available CeO₂ (Sigma-Aldrich) was selected for comparison with the HSA-CeO₂.

2.2. Catalyst Characterization. The surface area of the samples, using the multipoint Brunauer, Emmett and Teller (BET) analysis method, was measured by N₂ adsorption at −196 °C, using an Autosorb-1 Quantachrome flow apparatus. The samples were dehydrated in vacuum at 250 °C overnight before surface area measurements. Pure HSA-CeO₂ prepared using a Pluronic template-assisted synthesis method yielded a surface area of 202 m²/g, whereas the surface area for the commercial ceria is 40 m²/g.

2.3. Catalytic Reaction. A micro catalysis testing unit of the laboratory scale was utilized for examining the performance of the heterogeneous solid catalyst in the dehydrogenation of ethylbenzene with CO₂ as an oxidant. There was a vertically installed U-tube in the fixed bed reactor made of quartz with 4 mm of internal diameter, 350 mm of length, and the reaction temperature was adjusted within the range of 400–500 °C by using electric heaters and the programmable temperature controller of an Zeton Altamira (AMI-200) instrument. The dehydrogenation catalyst (100 mg, 60–80 mesh) was mixed with 200 mg of quartz beads with a similar size, filled into the reactor, and pretreated for 1 h at 400 °C with 5% O₂/Ar gas prior to performing a reaction. Liquid ethylbenzene was supplied by means of a motorized syringe pump (New Era pump system, NE1000) into a heated line where it vaporized in the carrier stream. Ethylbenzene was introduced as a reactant (2.2 μmol/min), CO₂ as oxidant (5 mL/min), and Ar as the carrier (15 mL/min), giving a total flow rate of ~20 mL/min and a CO₂/ethylbenzene ratio of 100:1. The reactants had been mixed and preheated at 150 °C before the reactant was supplied into the reactor. The reactants and products were analyzed using a continuously sampling quadrupole mass spectrometer (QMS; Pfeiffer-Balzers Instruments), followed by a gas chromatograph (Buck Scientific) equipped with a flame ionization detector. For analysis of the products, a HP-innax column (30 m long, 0.32 mm i.d, and 0.25 μm film thickness) was employed. The main products analyzed were styrene, benzene, toluene, and methane. Other gas products such as H₂, CO, and CO₂ were monitored by the mass spectrometer. The total carbon balance closed to within ±5%.

2.4. In Situ Spectroscopy. Infrared spectra were collected using a Thermo Nicolet Nexus 670 spectrometer in diffuse reflectance mode (DRIFTS). A Pike Technologies HC-900 DRIFTS cell with nominal cell volume of 6 mL was used. The powder sample (50 mg) was placed in the sample cup with a porous screen at the bottom surface, allowing the gas to uniformly pass through the catalyst from top to bottom. A feed gas mixture, controlled using mass flow controllers, was supplied at a flow rate of 10 mL/min. Prior to DRIFTS measurements of adsorption or reaction, the CeO₂ samples were first calcined in a flow of 10% O₂/He at 500 °C for 0.5 h and then cooled to room temperature. A background spectrum of the calcined sample was recorded in flowing He at each temperature used for analysis. These background spectra were subtracted from subsequent sample spectra obtained at the same temperatures. The DRIFTS spectra were collected from 4000 to 650 cm⁻¹, accumulating 100 scans at a 4 cm⁻¹ resolution.

For Raman studies, the sample was pretreated in an in situ Raman catalytic reactor (Linkam CCR1000). Raman scattering was collected via a customized ellipsoidal mirror and directed by a fiber optics bundle (Princeton Instruments) to the spectrograph stage of a triple Raman spectrometer (Princeton Instruments Acton Trivista 555). Edge filters (Semrock) were used in front of the UV–vis fiber optic bundle to block the laser irradiation. The 442 nm excitation (∼5 mW at sample) was emitted from a HeCd laser (Melles Griot). A UV-enhanced liquid N₂-cooled CCD detector (Princeton Instrument) was
employed for signal detection. The Raman reactor sits on an XY stage (Prior Scientific, OptiScan XY system) and translates in raster mode while collecting the spectrum. The fast translation has been shown to be able to minimize any laser damage of the surface adsorbates and the samples. Cyclohexane was used as a standard for the calibration of the Raman shifts.

For both IR and Raman in situ spectroscopy, experiments were performed to investigate the ethylbenzene adsorption, desorption; ODH; and styrene adsorption, desorption. For each experiment, the sample was first calcined (5% O$_2$/Ar, 10 mL/min) at 450 °C for 30 min in the in situ cell, and then decreased to room temperature and purged by He or Ar (10 mL/min) for 30 min before exposure to reactants. For styrene experiments, ~1 μL of neat styrene was dropped into the catalyst at room temperature prior to re-establishing the purge. A bubbler was used to introduce gas phase ethylbenzene into the reactant stream.

3. RESULTS AND DISCUSSION

3.1. Catalytic results. The catalytic performance of HSA-CeO$_2$ and of commercial CeO$_2$ was measured under steady state conditions between 400 and 500 °C using a CO$_2$/ethylbenzene molar ratio of ~100. A pretreated sample was held at a sequence of increasing temperatures, for 2 h at each temperature, and the reactants and products were analyzed repeatedly and averaged. In all cases, the major product in the reaction is styrene (selectivity >80%), accompanied by a small amount of benzene, and toluene as byproducts (<20%). Ethylbenzene conversion ($X_{EB}$), product selectivity ($S_p$) and styrene yield ($Y_{ST}$), are shown in the following equations:

$$X_{EB} = (1 - \text{ethylbenzene out/ethylbenzene in}) \times 100$$

$$S_p = \left(\frac{\text{product out}}{\text{ethylbenzene in} - \text{ethylbenzene out}}\right) \times 100$$

$$Y_{ST} = \frac{X_{EB} \times S_p}{100}$$

Pure HSA-CeO$_2$ (Figure 1a) gives a higher ethylbenzene conversion compared with the commercial ceria (Figure 1b) in the whole temperature range. The ethylbenzene conversion increased with temperature over the two catalysts. The highest catalytic performance was obtained at 500 °C with ethylbenzene conversion of ~85%, styrene selectivity of ~90% and yield of ~80% over the HSA-CeO$_2$. The reaction rates of ethylbenzene at 450 °C based on the surface areas are similar for the two catalysts, as shown in Table 1, which indicates that the main reason for the higher activity and yield of styrene over HSA-CeO$_2$ is the larger surface area of the HSA-CeO$_2$. In previous reports of K promoted-Fe$_2$O$_3$ catalysts, the ethylbenzene conversion was typically measured at higher temperature (580–600 °C) using steam as a diluent and yielded specific activity of 18 × 10$^3$ μmol/(h·g). Although K-Fe$_2$O$_3$ catalysts have higher specific activities under those conditions compared with the HSA-CeO$_2$ (350 μmol/(hr·gm), the lower temperatures and the use of CO$_2$ as a diluent has advantages.

To understand the role of CO$_2$ in the dehydrogenation of ethylbenzene, the reaction was also conducted without CO$_2$ for the HSA-CeO$_2$ catalyst. Table 2 compares the catalytic results for the ethylbenzene dehydrogenation to styrene at 400–500 °C under steady state in the presence and absence of CO$_2$ in the flow. In the absence of CO$_2$, the dehydrogenation reaction...
also occurred and produced a lower amount of styrene. This suggests that the direct dehydrogenation reaction of ethylbenzene to styrene occurred over the HSA-CeO₂ catalyst; however, both the ethylbenzene conversion and styrene yield were increased by the addition of CO₂.

Aging tests in CO₂ were conducted as shown in Figure 2 for a freshly pretreated HSA-CeO₂ at 450 °C. Figure 2 shows that although the measured ethylbenzene conversion initially decreased, it stabilized after 2 h, and the styrene yield was nearly constant over the 12 h test. The initial decrease in the apparent conversion may be attributed in part to initial retention of ethylbenzene by surface adsorption, including formation of polystyrene (see below). The nearly stable styrene yield indicates the steady reaction rate without catalyst deactivation.

QMS measurements of the H₂ produced during the reaction are shown in Figure 3, and these indicate that H₂ was produced during the dehydrogenation reaction over the HSA-CeO₂ in both the presence and absence of CO₂. However, less H₂ was observed at the same temperature when CO₂ was present, which might be due to the oxidation of the produced H₂ by CO₂ that is, a reverse water gas shift reaction. To further confirm this reaction route, we also tested the reverse water gas shift reaction over the HSA-CeO₂ by flowing CO₂ and H₂ over pretreated HSA-CeO₂ within the same temperature range used for the ethylbenzene dehydrogenation. A molar ratio CO/H₂ of 2:1 was used with a total flow rate of 25 mL/min and Ar as the carrier gas (100 mg sample; CO₂: 1.6%). The observed conversion of CO₂ to CO increased with increasing temperature, and the highest conversion of CO₂ to CO is around 10% at 500 °C, close to the predicted equilibrium value for reverse water gas shift reaction. For example, the ethylbenzene ODH reaction with CO₂ over ceria by the two-step pathway must occur. However, on the basis of the current data, it is not possible to eliminate the possibility that the one-step pathway, reaction 5, may occur simultaneously and the relative importance of these two routes can not be determined.

To further clarify the exact role of CO₂ in the ethylbenzene ODH reaction and explain how the CO₂ interacts with the surface of the ceria and favors the activity and styrene yield, in situ DRIFTS and Raman studies were further carried out.

3.2. In Situ DRIFTS. 3.2.1. Styrene Adsorption—Desorption on HSA-CeO₂. Figure 4 shows the infrared spectra of styrene adsorbed onto a calcined sample of HSA-CeO₂ at room temperature and followed by sequential heating in He to higher temperatures. The spectrum obtained at room temperature is consistent with adsorbed styrene as observed previously. The skeletal C—C stretching modes of the aromatic ring occur at 1600, 1540, 1500, 1450, 1200, 1081, and 1020 cm⁻¹, as indicated by markers in Figure 4. The C—H deformation and C—H bending of the aromatic ring appeared at 1176 and 1155 cm⁻¹.
cm$^{-1}$. The four bands above 3000 cm$^{-1}$ (3083–3010 cm$^{-1}$) are assigned to the C–H stretches in the adsorbed styrene. The vinyl group of styrene has several characteristic bands: the C–H out-of-plane bending modes of the vinyl group, −CH=CH$_2$ and −CH$_2$=CH$_2$ at 910 and 990 cm$^{-1}$ respectively; their overtones 1820 and 1980 cm$^{-1}$; and the C–H in-plane bending modes of the vinyl group at 1400 cm$^{-1}$. The bands at 1370 cm$^{-1}$ is due to the CH$_2$ in-plane bending of the vinyl group. A band of 1629 cm$^{-1}$ is associated with the vinyl C=C=C of the styrene. The assignment of the 1270 cm$^{-1}$ band is not clear, but it is present at all temperatures, so we assign it to an out-of-plane C–H bending, possibly of the aryl H.

Heating the adsorbed styrene to 200 °C leads to prominent changes in the spectrum. These changes are due to the combined effects of desorption and coupling (oligomerization) to form polystyrene. The strongest evidence for the formation of polystyrene is observed in the C–H stretching region, where prominent peaks at 2846 and 2931 cm$^{-1}$ due to the CH$_3$ and CH vibrations of the polystyrene consistent with previous IR data. A new band at 2721 cm$^{-1}$ shows a trend similar to the bands of 2931 and 2846 cm$^{-1}$ and is suggested to be C–H stretching of polystyrene. In addition, the peak at 1600 cm$^{-1}$ for styrene shifts to 1595 cm$^{-1}$ and strengthens to form a prominent peak. This feature is also typical of the polystyrene. Styrene persists on the surface but decreases due to desorption and its polymerization. Evidence of styrene is the vinyl ν(C=C) (1629 cm$^{-1}$), the bending modes, −CH=CH$_2$ and −CH$_2$=CH$_2$ (910, 990) and their overtones (1820 and 1980 cm$^{-1}$). Aromatic skeletal modes (1600, 1500, 1450, and 1200 cm$^{-1}$) decrease with temperature due to desorption of styrene and effects of polymerization.

As the temperature is increased to 400 °C, the C–H stretching bands of the polystyrene (2931, 2846, and 2721 cm$^{-1}$) decrease in intensity. Simultaneously, bands due to vinyl (1880, 1820, 990, and 910 cm$^{-1}$) decrease with increasing temperature and vanish at 500 °C. By 500 °C, only the bands at 3058, 1595, 1270, and 1155 cm$^{-1}$ persist and are assigned to a highly dehydrogenated carbon (coke) remaining on the surface of the ceria. All features due to vinyl groups disappear, along with all of the CH stretching modes indicative of dehydrogenation of all surface species, consistent with coke.

Summarizing, the above results show that at room temperature most of the styrene adsorbs as monomers, while the result of heating to higher temperatures (200–450 °C) causes coupling of the styrene to form polymer on the ceria. Styrene monomer is present on the surface throughout this range, as indicated by the persistent vinyl bands. Continued coadsorption of styrene and polystyrene suggests that reverse decomposition of polymer to monomer continues, following reaction 7.

It has been reported that polystyrene can depolymerize to styrene in the temperature range of 200–450 °C during the heating process, which is consistent with our results. After heating at 500 °C, no C≡C band and vinyl group were observed, indicating most of the surface species are polymerized and depolymerization has stopped. The disappearance of the CH$_4$ and CH stretching at 2931 and 2846 cm$^{-1}$ indicates nearly complete dehydrogenation of the alkyl H with possible coupling. Lack of available H prevents desorption and depolymerization, leaving only a highly dehydrogenated carbonaceous adsorbate typical of coke. Details of this will be discussed in the following Raman spectrum.

### 3.2.2. Ethylbenzene Adsorption—Desorption on HSA-CeO$_2$

The activity results (Table 2) indicate that over HSA-CeO$_2$, the dehydrogenation reaction of ethylbenzene to styrene can occur in the absence of CO$_2$. To clarify the surface interaction of ethylbenzene with ceria in the absence of CO$_2$, infrared spectra were collected for ethylbenzene adsorbed onto HSA-CeO$_2$ at 150 °C and followed by heating in He at various temperatures. These are shown in Figure 5. Following adsorption at 150 °C,
several bands characteristic of ethylbenzene were observed. The C–H stretches in the aromatic ring occur at 3058 and 3020 cm$^{-1}$, whereas the bands at 2964, 2931, and 2873 cm$^{-1}$ are due to methyl and methylene CH stretches in the ethyl group.$^{26}$ Skeletal C–C stretching modes of the aromatic ring are visible at 1600, 1540, and 1500 cm$^{-1}$. Upon subsequent heating to 200 °C, several new IR bands appeared or became sharper at 1980, 1820, 1400, 1370, 1351, 1270, 1176, 1155, and 990 cm$^{-1}$. These bands were all seen in the spectra following styrene adsorption as discussed above and shown in Figure 4. In particular, the bands at 1980, 1820, 1629, and 990 cm$^{-1}$ are associated with the vinyl function of styrene. Appearance of these bands confirms that the direct dehydrogenation of ethylbenzene to styrene occurs over the surface of the HSA-CeO$_2$ catalyst, which is consistent with our activity test results.

The bands due to styrene generally increased in intensity with temperature at 300 °C but declined after heating to 400 °C or higher. At 500 °C, the C–H stretching bands are strongly decreased (less so for the aromatic stretch at 3064 cm$^{-1}$). This dehydrogenation is accompanied by a persistent band near 400 °C that can be associated with coke buildup, but several bands remain due to the C–C stretches (1595, and 1056 cm$^{-1}$) and C–H bending (1176 cm$^{-1}$) of the aromatic ring. Bands at 1351 and 1465 cm$^{-1}$ remain and are assignable to styrene oligomer.$^{27}$ This indicates that at higher temperature (500 °C), some of the styrene forms oligomers on the surface of the ceria during the direct dehydrogenation of ethylbenzene. A new band of 2127 cm$^{-1}$ appears at temperatures above 400 °C, which could be assigned to reduced ceria.$^{34}$ We may infer that during the reaction of direct dehydrogenation of ethylbenzene, some H$_2$ was produced with the styrene production. The resulting H$_2$ can react with the surface lattice oxygen on the ceria (reaction 8), leading to reduction of the ceria at temperatures as low as 500 °C.$^{35}$

$$\text{H}_2 + \text{O} \rightarrow \text{H}_2\text{O} \quad (8)$$

3.2.3. CO$_2$ Adsorption–Desorption on HSA-CeO$_2$. To clarify the role of CO$_2$ in the ethylbenzene ODH reaction and how it interacts with ethylbenzene on ceria, in situ DRIFTS spectra were collected for CO$_2$ adsorption on HSA-CeO$_2$ at 150 °C and followed by purging and heating in He at various temperatures. The results are shown in Figure 6. Several IR bands appearing at 1616, 1390, 1270, and 1176 cm$^{-1}$ are assigned to carbonate and bicarbonate formed from CO$_2$ adsorption at 150 °C on the ceria surface.$^{36,37}$ These bands decrease in intensity with increasing temperature and become very weak at 400 °C. These results prove that CO$_2$ can reactively adsorb on ceria at low temperatures, but these decompose and desorb at higher temperatures. This loss of carbonate may contribute to the increased ODH activity above 400 °C because loss of carbonate releases available surface sites for ODH reaction.

3.2.4. Reaction of Ethylbenzene + CO$_2$ over HSA-CeO$_2$. The reaction between CO$_2$ and ethylbenzene on the surface of HSA-CeO$_2$ was investigated by in situ DRIFTS. Spectra were collected at various temperatures while continuously flowing both ethylbenzene and CO$_2$ over the HSA-CeO$_2$. As can be seen in Figure 7, bands due to gas phase CO$_2$ (2362, 2319 cm$^{-1}$) were observed at 150 °C$^{38}$ along with features due to carbonates (1616, 1390, 1216 cm$^{-1}$), as seen in Figure 6. Several peaks due to adsorbed ethylbenzene also appeared (1540, 1500, 1270, 1056, and 1020 cm$^{-1}$) at the same time. At temperatures higher than 300 °C, new bands assignable to styrene (1980, 1820, 1400, 1370, 1300, 1176, 1155, 990, and 910 cm$^{-1}$) appeared,$^{39}$ demonstrating that the ethylbenzene dehydrogenated to styrene while in the presence of CO$_2$. Meanwhile with the elevation of temperature, the bands due to carbonate (1616 and 1216 cm$^{-1}$) gradually disappeared, and bands due to adsorbed ethylbenzene (1595 and 1176 cm$^{-1}$) became clearer. This result shows that both ethylbenzene and CO$_2$ can adsorb on the HSA-CeO$_2$ simultaneously at low temperatures, but the adsorbed carbonates might block the active ceria sites, thus inhibiting ODH reaction at low temperatures. At temperatures of 300 °C and higher, the carbonate decomposes and desorbs from the surface of the catalyst, and then the adsorbed ethylbenzene interacts with the ceria to produce styrene. Meanwhile, the band due to the

![Figure 6. DRIFTS spectra of CO$_2$ adsorbed on HSA-ceria at 150 °C and followed by desorption in He (10 mL/min) at various temperatures. Reaction conditions: 5% CO$_2$ in He exposed to the catalyst at 150 °C for 30 min, followed by purging in He at various temperatures.](image)

![Figure 7. In situ DRIFTS spectra of ODH reaction of CO$_2$ + ethylbenzene over HSA-ceria at various temperatures. Reaction conditions: 0.2% ethylbenzene; CO$_2$, 2.5 mL/min; He, 7.5 mL/min as carrier gas adsorbed on the catalyst at 150 °C for 30 min, followed by heating in reactants at various temperatures.](image)
reduced ceria at 2127 cm$^{-1}$ appeared, suggesting that H$_2$ produced by the dehydrogenation of ethylbenzene reacted with the surface oxygen on ceria, causing its reduction. The ethylbenzene first dehydrogenated to styrene and H$_2$, and then the H$_2$ was available to react either with lattice O or with CO$_2$ via the reverse water gas reaction. To further clarify the coking formation during the ODH reaction of ethylbenzene and how CO$_2$ interacts with the coke, in situ Raman spectra was explored.

### 3.3. In situ Raman

#### 3.3.1. Styrene Adsorption–Desorption on Ceria in Ar

Raman spectra of adsorbed styrene on HSA-CeO$_2$ were collected at room temperature, followed by desorption in Ar at various temperatures. As shown in Figure 8, the Raman bands of the pure HSA-CeO$_2$ were observed at 345, 466, 556, 592, and 1714 cm$^{-1}$ as a result of second-order transverse acoustic (2TA) mode, E$_{2g}$ mode of the CeO$_2$ fluorite phase, D band due to the presence of oxygen vacancies of reduced ceria, defect-sites-induced D mode, and second-order longitudinal optical (2LO) modes of the ceria, respectively.

Raman bands at 1005, 1185, 1200, 1321, 1417, 1498, 1600, and 1629 cm$^{-1}$ due to the styrene adsorption were observed at room temperature after introducing styrene in Ar while some of the ceria bands (345, 556, 592, and 1714 cm$^{-1}$) were attenuated by the styrene. The observed bands could be assigned to C–H bending of an aromatic ring (1185, 1200 cm$^{-1}$), the $\equiv$CH$-$ and $\equiv$CH$_2$ deformation (1321, and 1417 cm$^{-1}$) C–C stretch of the aromatic ring (1005, 1033, 1498, 1600 cm$^{-1}$), and vinyl C=C stretches (1629 cm$^{-1}$). It is significant that the C=C stretching at 1629 cm$^{-1}$ disappeared at temperatures above 200 °C because this suggests polymerization. Meanwhile, the C–C stretches of aromatic rings (1005, 1498 cm$^{-1}$) increased, the peak at 1600 cm$^{-1}$ shifted to 1595 cm$^{-1}$, and a new band at 1447 cm$^{-1}$ appeared.

The band at 1447 cm$^{-1}$ is usually assigned to polyolefin. Comparison of the spectrum at 200 °C to that reported polystyrene confirms the bands of 1005, 1185, 1447, 1498, and 1595 cm$^{-1}$ observed are due to the formation of polystyrene; however, upon heating to 400 °C, the bands of polystyrene decreased, while a new band at 1330 cm$^{-1}$ increased in intensity and the band at 1595 cm$^{-1}$ shifted to 1580 cm$^{-1}$, indicating the formation of new species. The bands at 1580 and 1330 cm$^{-1}$ have been reported as graphite-like coke. This suggests that the polystyrene must be the intermediate for the formation of coke on the surface of the HSA-CeO$_2$ at higher temperatures (>400 °C). After heating to 500 °C, the bands due to polystyrene almost vanished, and the two bands at 1330 and 1580 cm$^{-1}$ were still present, which indicates that polystyrene further dehydrogenated to coke deposited on the ceria surface. These transformations in the adsorbed styrene layer also affected the CeO$_2$ bands, which became clearer after heating to 200 °C as a result of partial desorption and polymerization of styrene and then diminished again above 400 °C as coke formed on the surface. Combined with our DRIFTS results of styrene adsorption–desorption, in Figure 4, we have found it is easy for styrene to polymerize and form polystyrene, whereas polystyrene was also able to decompose to styrene monomers in the temperature range of 200–450 °C, but at temperatures above 500 °C, the polystyrene further dehydrogenated to produce coke (reaction 9).

$\text{CH}_n \rightarrow \text{C}_n\text{H}_{2n+2} \rightarrow \text{C}_n\text{H}_m$  

(9)

#### 3.3.2. Ethylbenzene Adsorption–Desorption on Ceria in Ar

For comparison, Raman spectra of adsorbed ethylbenzene on HSA-CeO$_2$ were collected at room temperature and then heated in Ar at different temperatures, as shown in Figure 9.

After introducing ethylbenzene (0.2%) in Ar over the ceria at room temperature, new Raman bands due to ethylbenzene were still present, which correspond to the CCC deformation of the aromatic ring; the bands at 717 and 833 cm$^{-1}$ remained, followed by purging by Ar (10 mL/min) at various temperatures.
cm\(^{-1}\) are assigned to the CC stretch of the aromatic ring.\(^{28}\) Bands 1265, 1321, and 1391 cm\(^{-1}\) are due to the CH\(_2\) or CH\(_3\) deformation.\(^{38,41,46}\) Most of the Raman bands associated with ethylbenzene decreased in intensity with an increase in the temperature due to the desorption of ethylbenzene, whereas the bands at 1321, 1498, and 1567 cm\(^{-1}\) initially increased in intensity with temperature (100–300 °C) and then decreased and disappeared at higher temperatures (>400 °C). These three bands can be found in the Raman spectra of styrene adsorption in Figure 8.

In addition, the band at 1567 cm\(^{-1}\) has also been reported to relate to conjugated olefin,\(^{33,47}\) indicating that new species of styrene might have formed during the heating process of ethylbenzene. At 300 °C and above, the band at 1600 cm\(^{-1}\) shifted to 1595 cm\(^{-1}\), and the bands related to polystyrene, as we discovered in Figure 8 at 1167 and 1498 cm\(^{-1}\), were present, implying the formation of polystyrene. Some amount of styrene was formed in the heating process during the ethylbenzene desorption. This is consistent with our DRIFTS results in Figure 5. The produced styrene polymerized and formed some polystyrene on the surface of ceria. However, less coke was formed at 500 °C, and above, the band at 1600 cm\(^{-1}\) shifted to 1595 cm\(^{-1}\), signaling the formation of polystyrene. However, no significant graphite-like coke was observed. In addition, as found when heating ethylbenzene in Ar, the band intensity due to the defects sites on ceria (592 cm\(^{-1}\)) shifted to the oxygen vacancy band (556 cm\(^{-1}\)) with the temperature increase, indicating that the ceria was reduced by the dehydrogenation process.

For comparison, the in situ Raman spectra during the ethylbenzene dehydrogenation reaction in absence the of CO\(_2\) on HSA-CeO\(_2\) at different temperatures was collected; the results are shown in Figure 11. After introducing ethylbenzene/Ar over the ceria at 100 °C, several Raman bands due to ethylbenzene appeared (711, 821, 1005, 1167, 1265, 1321, 1391, 1447, 1498, and 1567 cm\(^{-1}\))\(^{28}\) along with the bands of ceria (345, 466, and 592 cm\(^{-1}\)). These Raman bands of ethylbenzene decreased in intensity with the temperature reaction. When the temperature increased to 400 °C, several bands related to polystyrene (1005, 1167, 1321, 1391 cm\(^{-1}\)) were observed, and the band at 1600 cm\(^{-1}\) shifted to 1595 cm\(^{-1}\), which indicates that some styrene might be produced and further polymerize to form polystyrene during the heating process. These bands of polystyrene vanished at temperatures above 500 °C, whereas two new bands at 1330 and 1580 cm\(^{-1}\) appeared at higher temperatures (>500 °C). The two bands have been observed in Figure 8 during styrene desorption and are reported as following ethylbenzene adsorption at 25 °C (Figure 9), but in addition, two new bands at 1238 and 1651 cm\(^{-1}\) were observed at 100 °C that are assigned to carbonates. These bands are related to the DRIFTS bands observed at 1216 and 1616 cm\(^{-1}\) (Figure 7) and indicate that both ethylbenzene and CO\(_2\) are coadsorbed on the surface. In addition, these two Raman bands vanished upon heating to 200 °C, which is consistent with our DRIFTS results. During the temperature elevation process, the bands due to ethylbenzene (717, 833, and 1265 cm\(^{-1}\)) decreased, and some bands related with styrene (1167, 1321, 1391, 1447, 1498, and 1567 cm\(^{-1}\))\(^{12}\) increased. As the temperature was increased to 400 °C, the bands assigned to polystyrene at 1005, 1167, 1321, 1391, and 1498 cm\(^{-1}\) were significant while the band at 1600 cm\(^{-1}\) shifted to 1595 cm\(^{-1}\), signaling the formation of polystyrene. However, no significant graphite-like coke was observed. In addition, as found when heating ethylbenzene in Ar, the band intensity due to the defects sites on ceria (592 cm\(^{-1}\)) shifted to the oxygen vacancy band (556 cm\(^{-1}\)) with the temperature increase, indicating that the ceria was reduced by the dehydrogenation process.

![Figure 11](image)

**Figure 11.** In situ Raman spectra of ethylbenzene dehydrogenation reaction over HSA-eria in Ar at different temperatures. Reaction conditions: 0.2% ethylbenzene; Ar, 10 mL/min as carrier gas pass over the catalyst at 100 °C for 30 min, followed by heating in reactants at various temperatures.
They prove that dehydrogenation of ethylbenzene over ceria in the absence of CO2 results in coke deposited on the surface of the HSA-CeO2. In addition, the peak intensity of ceria at 466 cm⁻¹ decreased, possibly due to the buildup of coke, and the band at 592 cm⁻¹ shifted to 556 cm⁻¹, indicative of reduction of ceria. In contrast, no significant coking was observed in the presence of CO2 during the ODH reaction over HSA-CeO2 at high temperature (Figure 10), which indicates that CO2 helps inhibit deposition of coke on the catalyst.

### 3.3.4. Oxidation of Coke on Ceria by CO2

In situ Raman spectra of the interaction between CO2 and the coked ceria sample were further explored to clarify the exact role of CO2 in ODH reaction of ethylbenzene. Figure 12 gives the Raman spectra of the coked ceria sample (after ethylbenzene dehydrogenation reaction in Ar at 600 °C).

#### Figure 12. Raman spectra of reoxidation process of coked ceria using CO2 at different temperatures. Coked ceria is from ethylbenzene dehydrogenation reaction in Ar at 600 °C.

The authors may conclude that, in the absence of CO2, coke is formed during the ethylbenzene dehydrogenation reaction over ceria. Introduction of CO2 may enhance the reaction in two ways: First, CO2 may react with the H evolved in the ethylbenzene dehydrogenation, by reverse water gas shift reaction, removing H2 from the reaction stream and favoring the dehydrogenation reaction. Second, the CO2 removes coke from the surface of ceria, thereby opening ceria sites. CO2 might interact with ceria and release CO and atomic O, which could oxidize the coke at high temperatures. Pulse experiments indicate that CO2 could also contribute to catalyst oxidation. Alternatively, the CO2 may more rapidly form carbonates as intermediates to the oxidation of the coke. DRIFTS during reaction (Figure 7) showed that the peak at 2127 cm⁻¹, characteristic of reduced ceria, is observed at 400–500 °C. This result indicates that although CO2 mainly oxidizes the produced H2 and the coke, it does not completely oxidize the reduced ceria under reaction conditions.

### 4. CONCLUSIONS

HSA-CeO2 synthesized via a template-assisted synthesis method has been shown to be an active and selective catalyst for ODH reaction of ethylbenzene to produce styrene by using CO2 as a soft oxidant. In the absence of CO2, ethylbenzene dehydrogenation reaction occurred over the HSA-CeO2, but graphite-like coke was formed on the surface of ceria. In the presence of CO2, the ethylbenzene ODH reaction must follow a two-step pathway in which ethylbenzene is first dehydrogenated to styrene and H2, and then CO2 reacts with H2 via the reverse water gas shift reaction, although the direct ODH of ethylbenzene by CO2 may also be possible. Addition of CO2 not only enhanced the ethylbenzene ODH reaction rate and styrene yield but also helped mitigate the coke deposition during the ethylbenzene ODH reaction. The coke deposit is formed from the polymerization of styrene and further graphitization in the absence of CO2, but in the presence of CO2, the coke is oxidized by CO2 and the deposition is effectively inhibited.

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**Notes**

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### REFERENCES


