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Short Communication

The dehydrogenation of ethylbenzene with CO_2 over $Ce_xZr_{1-x}O_2$ solid solutions

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ABSTRACT

With the purpose of changing the lattice structure of CeO_2 and improving the transmission capacity of lattice oxygen, $Ce_xZr_{1-x}O_2$ solid solutions with different Zr proportions were synthesized using a hydrothermal method and applied in oxidative dehydrogenation of ethylbenzene to styrene with CO_2 at 550 °C. The $Ce_{0.5}Zr_{0.5}O_2$ showed the highest activity with an ethylbenzene conversion of 55% and styrene selectivity above 86%. Analytical characterization showed that the lattice oxygen mobile capacity of $Ce_xZr_{1-x}O_2$ solid solutions was enhanced, corresponding to the order as $Ce_{0.3}Zr_{0.7}O_2 > Ce_{0.5}Zr_{0.5}O_2 > Ce_{0.7}Zr_{0.3}O_2 > CeO_2$. The oxygen storage/release capacity, higher surface area and pore distribution of Ce–Zr mixed oxides play important roles in the activity of ethylbenzene dehydrogenation to styrene with CO_2.

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1. Introduction

Styrene is an important raw material as it is the basis for petrochemical industry products, synthetic rubber and plastics [1,2]. To solve the limitation of the thermodynamic method, the dehydrogenation of ethylbenzene (EB) to styrene (ST) with CO_2 is thoroughly investigated [3–6]. In this process, using CO_2 is an effective way in CO_2 emission reduction [7,8]. It is important to develop new technology to prepare highly efficient catalysts. The process of oxidative dehydrogenation requires the participation of lattice oxygen, which is indispensable in maintaining the catalytic activity because the active material is reduced by the loss of lattice oxygen [9,10]. It is proven that the catalytic activity sharply decreased with a decrease in the amount of available lattice oxygen [11,12]. CO_2 was added as a soft oxidant in the process of ethylbenzene dehydrogenation, however, the strong deactivation of the catalytic process showed that CO_2 was not able to recover the active oxygen particles at the speed of consumption [13].

Lattice oxygen could be added by CO_2 in the dehydrogenation reaction process [14]. Ceria of the CaF_2 structure has excellent oxygen storage/release capacity (OSC) [15]. The OSC of ceria is well-associated with the presence of oxygen vacancies. More oxygen vacancies would lead to increased OSC and enhance redox properties in the catalyst [16]. Ceria-based mixed oxides are able to exchange very large amounts of oxygen compared to ceria [17] (such as $Ce_xFe_{1-x}O_2$ and $Ce_xZr_{1-x}O_2$). Furthermore, oxygen in the $Ce_xZr_{1-x}O_2$ samples is predominantly exchanged via a multiple hetero-exchange mechanism involving surface dioxygen (or particles) species such as superoxides and peroxides [18]. The addition of other metal oxides can render the instability of the ceria fluorite phase, which is an important phase for catalysis as its oxygen ions are mobile and oxygen deficiency is accommodated by oxygen vacancies [19]. The transmission capacity of lattice oxygen plays an essential role in the process of oxidative dehydrogenation; while the oxygen vacancies are beneficial to CO_2 activation [20,21]. Han [22] used the XRD and XPS (X-ray photoelectron spectroscopy) to study the CeO_2 catalyst for the dehydrogenation of EB reactions. The CeO_2 catalyst was a mixed valence oxide, which contained both Ce^{3+} and Ce^{4+} ions in H_2, CO (strong reducer) and H_2O (weak oxidizer) atmosphere. The dynamic equilibrium CeO_2–CeO_{2-x} $(0 < x < 0.3)$ took place on the surface of the CeO_2 catalyst. The rapid oxygen exchange between the Ce^{4+}/Ce^{3+} redox as well as the improvement in the OSC of ceria helped the iron to keep its high shift activity [23]. Thus, ceria-based mixed oxides such as $Ce_xZr_{1-x}O_2$ solid solutions can be used in the dehydrogenation of ethylbenzene to styrene with CO_2 [24,25].

In this research, the effect of different Zr^{4+} proportions on the structure of CeO_2 and activity in the dehydrogenation of ethylbenzene were investigated. The crystal structure, textural characteristics, the OSC and redox properties of $Ce_xZr_{1-x}O_2$ were studied, focusing on the CO_2 activation and oxygen vacancy migration as a function of the composition of the mixed oxides. We were also interested in investigating whether

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lattice oxygen of doping oxides played an important role in enhancing the activity of the oxidative dehydrogenation of EB to ST with CO_2.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared using a hydrothermal method. Aqueous solutions of both $Ce(NO_3)_3\cdot 6H_2O$ and $Zr(NO_3)_3\cdot 5H_2O$ were adjusted using deionized water so that the concentrations of cerium and zirconium in the respective solutions were 0.25 mol/L. Aqueous ammonia (10%) was added as a precipitation agent while stirring until a pH of 10 was reached. After stirring for a further 3 h, the solution was transferred into a PTFE-lined stainless steel autoclave and aged under static conditions at 110 °C for 72 h. Finally, the precipitate was recovered by centrifugation and washed extensively with deionized water. After drying at 120 °C for 10 h, it was calcined at 550 °C for 6 h to be as-synthesized catalyst $Ce_{1-x}Zr_xO_2$. $Ce_{0.7}Zr_{0.3}O_2$, $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.3}Zr_{0.7}O_2$ are denoted as CZ30, CZ50 and CZ70 respectively in this study.

2.2. Catalyst characterization

The crystal structures of catalysts were recorded on a D/Max-3B Rigaku X-ray diffractometer (XRD) equipped with Cu-Kα radiation ($\lambda = 0.15406$ nm) using a pressed powder pellet method. The applied voltage and current were 30 kV and 40 mA, respectively. The samples were scanned from 5 to 85° at a scan rate of 8°/min.

Physical adsorption characteristics of the catalyst were investigated by a JW-BK122W physical adsorption instrument with N_2 as the adsorbate at −196 °C. The samples were activated for 2.5 h at 300 °C in a vacuum. The surface area of the catalyst was measured by the BET method, and the Barrett–Joyner–Halenda (BJH) calculation was used for pore distribution.

Raman spectroscopic data were obtained using a Renishaw inVia micro laser Raman spectrometer, Ar^+ laser (514.5 nm wavelength), with an output power of 4 mW, scanning range of 100–2000 cm^{-1}, and a 10 s exposure time.

The reduction behavior of the composite oxides was investigated using a hydrogen temperature-programmed reduction (H_2-TPR) process in a Micromeritics Autochem 2920 instrument. The samples were performed from 60 to 800 °C with a heating rate of 10 °C/min under 50 mL/min flow of 10 vol.% H_2 in argon. The oxygen storage capacity (OSC) was determined by H_2–O_2 titration. The samples were pre-treated for 30 min with 3 vol.% O_2 in helium at 550 °C, then pulsed with 10 vol.% H_2 in argon until catalyst saturation (loop volume was 0.55 cm^3).

2.3. Catalyst activity evaluation system

The reaction was carried out in a fix-bed down-flow stainless steel type reactor (i.d. 8 mm × 560 mm) operated at an atmospheric pressure. The EB feed rate was controlled by a micropump (American SSI Company). A 725 mg catalyst was placed into the center of the reactor using quartz wool plugs. The average particle size of the catalyst was 0.3–0.45 mm. The reaction temperature was 550 °C, EB flow rate was 0.01 mL/min, and the molar ration of CO_2 to EB was 20. The reaction products were analyzed on-line by a TianMei 7890 II gas chromatography equipped with an FID and TCD using TDX-01 packed columns. The peak area normalization method was used for quantitative analysis of products. Benzene is the standard sample (sensitivity factor sets at 1).

$$\text{Ethylbenzene conversion} = 1 - \frac{ethylbenzene_{out}}{(ethylbenzene + styrene + toluene + benzene)_{out}}$$

$$\text{Styrene selectivity} = \frac{styrene_{out}}{(styrene + toluene + benzene)_{out}}$$

where $ethylbenzene_{out}$ or $styrene_{out}$ stands for the amount of ethylbenzene or styrene in the products.

3. Results and discussion

3.1. Characterization

The textural characteristics of $Ce_{1-x}Zr_xO_2$ mixed oxides were depicted in Table 1 and Fig. 1. The nitrogen adsorption–desorption isotherms of $Ce_{1-x}Zr_xO_2$ catalyst were found to be Type IV and exhibited a H2 hysteresis loop (Fig. 1), which indicated the mesoporous nature of the catalysts. The BET surface area of pure CeO_2 is low and the mean pore size is around 10 nm. The addition of Zr can obviously enlarge the surface area of CeO_2 by more than double and decrease the mean pore radius to 3.7 nm, which may be in favor of CO_2 adsorption and activation [26]. An increase in the surface area was observed with the Zr proportion increasing from 0.3 to 0.7 and the maximum specific surface area was observed at CZ70. The mean pore radius of $Ce_{1-x}Zr_xO_2$ was about 3.7 nm, but the pore distribution of CZ50 was very different from CZ30 and CZ70. CZ50 had a very narrow pore distribution of around 3.6 nm, while CZ30 and CZ70 had a wider pore distribution ranging from 3 to 10 nm. Since the ionic radius of Zr^{4+} (0.084 nm) is smaller than that of Ce^{4+} (0.097 nm), the theoretical substitution of 50% of cerium by zirconium in CeO_2 can give a $(R_{Zr4+} + R_{Ce4+})/R_{O2-}$ ratio of 0.73 and a stable $Ce_{0.5}Zr_{0.5}O_2$ solid solution [27]. The narrow pore size distribution of CZ50 suggested the uniform structure of CZ50, which may be beneficial for the activity in dehydrogenation.

The XRD patterns of pure CeO_2, CZ30, CZ50 and CZ70 were plotted in Fig. 2. According to JCPDS, the XRD patterns of pure CeO_2 had a typical fluorite structure within the cubic phase with characteristic diffraction peaks at 28.6, 33.2, 47.5 and 56.4°, corresponding to the CeO_2 (111), (200), (220) and (311) planes. When Zr doped into the CeO_2 crystal structure, the XRD patterns of $Ce_{1-x}Zr_xO_2$ were similar to the cubic phase of CeO_2, with no characteristic ZrO_2 peaks observed. Some inhomogeneous distribution of ceria and zirconia cannot be completely ruled out. In comparison with the characteristic diffractions of CeO_2, the corresponding peaks for the $Ce_{1-x}Zr_xO_2$ progressively shifted to higher positions with the increase of Zr proportions. Moreover, the intensity of the $Ce_{1-x}Zr_xO_2$ peaks was lower than that of CeO_2. Also, with an increase in Zr doping, the intensity of $Ce_{1-x}Zr_xO_2$ decreased. This implied the formation of solid solutions, which is a consequence of a better arrangement of the atoms into the framework of pure CeO_2 and the decreased number of lattice defects [28]. The ionic radius of Zr^{4+} (0.084 nm) was slightly smaller than that of Ce^{4+} (0.097 nm). Consequently, the lattice parameter of the solid solution was decreased with the insertion of more Zr^{4+} into the CeO_2 lattice. The crystal sizes of all the $Ce_{1-x}Zr_xO_2$ calculated by the Scherrer formula were around 11 nm, indicating a nano-crystalline nature of the solid solutions. The more the Zr loading was, the smaller the crystal size of the $Ce_{1-x}Zr_xO_2$ solid solutions would be. Decrease in the crystallite sizes of $Ce_{1-x}Zr_xO_2$ than pure CeO_2 (15.8 nm) suggested that doped zirconia could restrain the increase of the crystal size of Ce–Zr oxides.

Raman characterization has also been carried out and the results as shown in Fig. 3 supported the XRD findings. CeO_2 and $Ce_{1-x}Zr_xO_2$ all exhibited an intense Raman band at 462 cm^{-1} and a weak and broad

Table 1
The textural characteristics of $Ce_{1-x}Zr_xO_2$ catalysts.

Catalyst	Crystallite size[a] (nm)	S_{BET} (m^2/g)	Mean pore size (nm)	OSC[b] (μmol/g)
CeO_2	15.8	47.0	10.7	97
CZ30	11.4	124.8	3.7	164
CZ50	10.9	131.9	3.6	394
CZ70	10.4	140.4	3.7	438

[a] Calculated on the basis of the X-ray diffraction peaks.
[b] By H_2–O_2 titration.

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