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Short communication

# Optimum ratio of K<sub>2</sub>O to CeO<sub>2</sub> in a wet-chemical method prepared catalysts for ethylbenzene dehydrogenation



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ABSTRACT

ity, but also prolonged the life cycle of catalysts.

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### 1. Introduction

Styrene, a basic raw material in petrochemical industry, is mainly produced via ethylbenzene dehydrogenation (EBDH) reaction. Traditionally, Fe<sub>2</sub>O<sub>3</sub> catalysts promoted with potassium are utilized to catalyze the reaction under superheated steam circumstance. However, excess superheated steam, high reaction temperature and rapid catalyst deactivation (resulting from coke formation) led to grim economic effect for the traditional industrialized route of EBDH [1–3]. Therefore, researchers attempted to search effective EBDH catalysts that can be used under facile conditions (low ratio of steam to ethylbenzene, low temperature and the catalysts should have long service life) [4].

Recent studies have shown that transition metal promoters, such as MgO and CeO<sub>2</sub>, could improve the catalytic activities of  $Fe_2O_3-K_2O$  based catalysts [5–12]. CeO<sub>2</sub> cannot only accelerate styrene formation, but also prevent potassium loss and prolong the service life of catalysts [8,10]. The potential mechanism is considered to be that CeO<sub>2</sub> in catalysts plays a role of oxygen transporter, which is essential to catalyzing EBDH. A two-step exchange mechanism for the diffusion of oxygen in CeO<sub>2</sub> is described in Fig. S1 (Supporting information) [11,12]. Furthermore, potassium ferrites (e.g.,  $K_2Fe_2O_{34}$ ) are the active phases in the catalysts and their transformation states strongly affect the catalytic activities, while CeO<sub>2</sub> facilitates the formation of active phases and stabilize them under reaction conditions at a low water ratio. Moreover,

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CeO<sub>2</sub> takes part in the Fe<sup>3+</sup> + e<sup>-</sup>  $\rightarrow$  Fe<sup>2+</sup> redox process and has an impact on the redox characters of the catalysts, thus affecting the ethylbenzene conversion and styrene selectivity [10,13]. However, it does not mean that higher CeO<sub>2</sub> content leads to better catalytic activity, because Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O components are also critical to catalysts (a higher

Fe<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-CeO<sub>2</sub> catalysts with various ratios of K<sub>2</sub>O to CeO<sub>2</sub> were prepared by the wet-chemical method. Their

phase compositions, reducibility, valence states of elements and catalytic activities for ethylbenzene dehydroge-

nation were studied. The results demonstrated that when the weight ratio of  $K_2O$ : CeO<sub>2</sub> was 1.40, the catalyst had

highest ethylbenzene conversion and styrene selectivity, which were attributed to the optimization of active

phase content and electron transfer ability, etc. Further, higher CeO<sub>2</sub> content not only enhanced styrene selectiv-

timum proportions of them should be discussed. In our laboratory, we found that when the fraction of Fe<sub>2</sub>O<sub>3</sub> was about 72.15 wt.%, the prepared catalysts possessed relatively high activity, so in the present work, we attempted to study the effect of various ratios of K<sub>2</sub>O to CeO<sub>2</sub> on the catalysts with fixed contents of Fe<sub>2</sub>O<sub>3</sub> and some other metal oxide components. A wet-chemical method was applied to fabricate Fe<sub>2</sub>O<sub>3</sub>–K<sub>2</sub>O–CeO<sub>2</sub> based catalysts. In order to find the optimum K<sub>2</sub>O/CeO<sub>2</sub> ratio for EBDH, comprehensive properties of the catalysts, including phase compositions, valence states of elements and catalytic activities, etc., were measured.

CeO<sub>2</sub> content means a lower content of Fe<sub>2</sub>O<sub>3</sub> or K<sub>2</sub>O). Therefore, the op-

#### 2. Experimental

#### 2.1. Catalyst preparation

The catalysts in the present work were composed of Fe<sub>2</sub>O<sub>3</sub> (72.15 wt.%), MgO (1.02 wt.%), MoO<sub>3</sub> (1.09 wt.%), K<sub>2</sub>O and CeO<sub>2</sub>. Notice that except for K<sub>2</sub>O and CeO<sub>2</sub>, we introduced the promoters of MgO and MoO<sub>3</sub>, because they could improve the styrene selectivity, and besides, MgO was also conducive to enhancing the stability of catalysts [7–9]. The mass ratio of K<sub>2</sub>O and CeO<sub>2</sub> in the catalysts was referred to K/Ce-*x*, where *x* represents the weight ratio of K<sub>2</sub>O to CeO<sub>2</sub>, and *x* was 1.75, 1.56, 1.40 and 1.12 (the digits were calculated based on the actual



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weight of K<sub>2</sub>O and CeO<sub>2</sub> in our catalysts. We prepared about 144 g catalysts and the weight of CeO<sub>2</sub> was set to be 13.5, 14.5, 15.5 and 17.5 g. Because the total mass fraction of K<sub>2</sub>O and CeO<sub>2</sub> was fixed, we could determine the weight of K<sub>2</sub>O and the ratio of K<sub>2</sub>O to CeO<sub>2</sub> in each catalyst). The preparation procedures were as follows: (1) Fe<sub>2</sub>O<sub>3</sub> powder was mixed with an aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·<sub>6</sub>H<sub>2</sub>O to obtain a metastable suspension; (2) poured the suspension into a mixed solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> slowly during stirring; (3) NH<sub>4</sub>OH was used to adjust the pH value of the mixture to 8 to get a heavy slurry; (4) aged the slurry for 1 h, dried at 120 °C for 4 h and calcined at 250 °C for 6 h in air to produce a paste, then extruded which to cylindrical strips ( $\Phi$ 3 × 5 mm); and (6) the final catalysts were obtained after the stripes were dried at 120 °C for 4 h and calcined at 850 °C for 4 h.

#### 2.2. Characterization of catalysts

Crystalline phases of the prepared catalysts were analyzed using a powder X-ray diffraction (XRD) analyzer. Valence states of elements in the catalysts were studied by X-ray photoelectron spectroscopy (XPS) measurements on a PHI Quantum-2000 instrument. Temperature programmed reduction of H<sub>2</sub> (H<sub>2</sub>-TPR) tests were performed under H<sub>2</sub>/Ar flow (30 ml/min; H<sub>2</sub> volume fraction was 5%) in a temperature range from 50 to 900 °C with a heating rate of 10 °C/min. Consumption amount of H<sub>2</sub> was continuously monitored by a thermal conductivity detector in a mass spectrometer.

## 2.3. Catalytic activity tests

The evaluation of the catalysts for EBDH was carried out using a cylindrical fixed-bed reactor with the diameter and length of 14 and 550 mm, respectively. 5 ml catalysts (about 6.5 g), with particle diameter of 0.71–1.18 mm, were loaded into the reactor for catalyzing EBDH reaction at 610 °C. During the reaction process, a mixture of gas of ethylbenzene (2.5 ml/h) and H<sub>2</sub>O (3.5 ml/h) was continuously injected into the reactor. Liquid hourly space velocity is 0.5/h. The end-products (containing styrene, toluene, benzene and ethylbenzene, etc.) were analyzed by gas chromatography with the assistance of a flame ionization detector.

# 3. Results and discussion

## 3.1. Phase compositions of the catalysts

CeO<sub>2</sub> VK<sub>2</sub>Fe<sub>22</sub>O<sub>34</sub> K/Ce-1.75 K/Ce-1.56 K/Ce-1.40 K/Ce-1.40 K/Ce-1.12 20 30 40 50 60 70 2-Theta (degree)

Fig. 1 shows the XRD spectra of various catalysts. Diffraction peaks due to  $K_2Fe_{22}O_{34}$  and  $CeO_2$  are detected from all the catalysts. The

Fig. 1. XRD patterns of the catalysts.

peaks arising from CeO<sub>2</sub> become stronger and sharper with a decreasing weight ratio of K<sub>2</sub>O to CeO<sub>2</sub>. Obviously, this can be attributed to the increasing content and grain size of CeO<sub>2</sub> [14]. While for the active phase of K<sub>2</sub>Fe<sub>22</sub>O<sub>34</sub>, the contents in K/Ce-1.56 and K/Ce-1.40 are higher than that in K/Ce-1.75 and K/Ce-1.12, through analysis by external standard method based on the corresponding diffraction peaks (Supporting information). Kotarba et al. has pointed out that the addition of CeO<sub>2</sub> had a positive influence on the formation of active phases [15], and this might be an important reason why K/Ce-1.75 catalyst does not possess highest K<sub>2</sub>Fe<sub>22</sub>O<sub>34</sub> content (K/Ce-1.75 has the lowest CeO<sub>2</sub> loading). Therefore, the K<sub>2</sub>O/CeO<sub>2</sub> ratio not only directly decides CeO<sub>2</sub> content in the catalysts, but also affects the amount of active phases.

# 3.2. H<sub>2</sub>-TPR tests

H<sub>2</sub>-TPR profiles are given in Fig. 2. Several peaks can be observed from each curve. For instance there are two strong peaks at about 450 and 750 °C. They are corresponding to the reduction process of Fe<sup>3+</sup> → Fe<sup>2+</sup> (low temperature peak) and Fe<sup>2+</sup> → Fe (high temperature peak) [4,6,16]. As a whole, higher CeO<sub>2</sub> content hinders the reducibility of Fe<sup>3+</sup> (Fe<sub>2</sub>O<sub>3</sub>) to Fe<sup>2+</sup> (Fe<sub>3</sub>O<sub>4</sub>) [10]. Furthermore, two intense hydrogen consumption bands can be observed at about 475 and 780 °C (the circled zones in Fig. 2). They result from the reduction of surface oxygen and bulk oxygen from CeO<sub>2</sub> (CeO<sub>2</sub> → Ce<sub>2</sub>O<sub>3</sub>) [13,17]. Because CeO<sub>2</sub> (Ce<sup>4+</sup>) and Ce<sub>2</sub>O<sub>3</sub> (Ce<sup>3+</sup>) have similar crystal structures (CaF<sub>2</sub>-typed), Ce<sup>4+</sup> and Ce<sup>3+</sup> are easy to coexist.

Copresence of Fe<sup>3+</sup> and Ce<sup>3+</sup> is possible on the basis of the reduction potential of the Fe<sup>2+/3+</sup> and Ce<sup>3+/4+</sup> couples. Significantly, the combined action of Fe<sup>3+</sup> and Ce<sup>3+</sup> plays a positive role in EBDH: during EBDH reaction,  $\alpha$ -hydrogen of ethylbenzene attacks the acid site of the catalysts (Fe<sup>3+</sup>) and simultaneously,  $\beta$ -hydrogen attacks the basic site (Ce<sup>3+</sup>), as shown in Fig. S2 [10,18,19], while positive charge on  $\alpha$ carbon at the transition state can be stabilized by the aromatic ring. Based on the point of view mentioned above, K/Ce-1.40 and K/Ce-1.12 catalysts may have better catalytic activity, because their relatively high CeO<sub>2</sub> content is beneficial for the keeping of Fe<sup>3+</sup> (instead of being reduced to Fe<sup>2+</sup>) and the coexisting of Fe<sup>3+</sup> and Ce<sup>3+</sup>.

# 3.3. XPS measurements

The reaction mechanism of EBDH catalyzed by  $Fe_2O_3-K_2O-CeO_2$  catalysts can be divided into two types: (a) direct dehydrogenation mechanism and (b) oxygen transfer dehydrogenation mechanism. Schematic expressions of these potential mechanisms are shown in Fig. S3. As metal oxide with variable valence,  $CeO_2$  can introduce a certain amount of oxygen vacancies to the catalyst, thus optimizing the activity of lattice oxygen, increasing electron transfer channels and making the dehydrogenation reaction easier to happen [10,20]. Therefore, it is necessary to detect the valence states of O and Ce elements in the catalysts.

Oxygen species have two spectral peaks in O 1s XPS spectrograms of Fe-K-Ce oxide based catalysts see Fig. 3: the peak at ~530.5 eV is ascribed to lattice oxygen of metal oxide and that at ~532.5 eV arises from adsorbed oxygen [17]. The Ce 3d XPS profiles in Fig. 4 are more complicated due to mixing of Ce 4f levels with O 2p states. Following the previous literature [17,20], the electronic transitions in Ce  $3d_{3/2}$ and Ce 3d<sub>5/2</sub> levels can be divided into several sets of features ground as U and V lines, respectively. The U'''/V''' doublet is associated with primary photo emission from Ce<sup>4+</sup>. The U"/V" and U/V doublets result from electron transfer from a filled O 2p orbital to an empty Ce 4f orbital. The U'/V' doublet is caused by photo emission from Ce<sup>3+</sup> cations. These evidences imply that cerium is present in the form of hybrid oxidation states of  $Ce^{3+}$  and  $Ce^{4+}$  [17,20]. This coincides well with the result obtained from catalyst TPR curves. Relatively, K/Ce-1.40 catalyst has stronger U"'/V"' and U/V doublets, corresponding to an effective electron transfer ability.



Fig. 2. H<sub>2</sub>-TPR profiles of the catalysts.

#### 3.4. Activity studies

The activities of the produced catalysts for EBDH are shown in Fig. 5 and Fig. S4. In the initial stage [7], the catalytic activities were not stable due to the formation of a thin layer of carbonaceous deposits. Thus for a better comparison, the activity data obtained after 12 h (reaction time) were considered. With decreasing K<sub>2</sub>O/CeO<sub>2</sub> ratio, both the conversion of ethylbenzene and the yield of styrene increase first and then decrease. As a consequence, K/Ce-1.40 catalyst exhibits the highest ethylbenzene conversion of 72.08% and styrene vield of 67.89%, while its styrene selectivity is slightly lower than that of the catalyst with K/Ce-1.12 (95.06% vs 95.43%). The catalytic activities of these catalysts are reasonable based on the above discussions of XRD, H2-TPR and XPS measurements. Besides, it is worth mentioning that the mechanical mixing method (using metal oxides as raw materials. Its simplicity makes it useful for industrial productions of EBDH catalysts) prepared catalysts with the same designed-compositions (metal oxide contents in theory) of K/Ce-1.12 displays moderate catalytic activity: the



Fig. 3. O 1s XPS profiles for the catalysts.

ethylbenzene conversion, styrene selectivity and styrene yield are only about 67.54, 94.45 and 63.79%, respectively. It indicates that the wetchemical method is superior for the preparation of EBDH catalyst.

In addition, we measured the conversion of ethylbenzene as a function of time-on-stream during EBDH reactions and found that for the catalysts with higher CeO<sub>2</sub> content, i.e., K/Ce-1.40 and K/Ce-1.12 catalysts, the conversion retention was ~98% after 90 h, while the catalysts containing lower CeO<sub>2</sub> content had notably reduced conversion as the reaction progresses (Fig. S4), once again suggesting that CeO<sub>2</sub> is beneficial for preventing potassium loss and prolong the service life of catalysts [8,10]. Except for that, as illustrated in Fig. 5, higher CeO<sub>2</sub> loading also improves the styrene selectivity.

# 4. Conclusions

 $Fe_2O_3-K_2O$  based catalysts with different ratios of  $K_2O$  to  $CeO_2$  were prepared. Their phase compositions, valence states of elements and



Fig. 4. Ce 3d XPS profiles for the catalyst.



**Fig. 5.** Catalytic activity of the prepared catalysts: conversion of ethylbenzene, selectivity toward styrene and yield of styrene. Each symbol stands for the specific value measured during EBDH reactions and the digits are the average values.

catalytic activities, etc., were studied. The results demonstrated that when the weight ratio of  $K_2O$  to  $CeO_2$  was 1.40, the catalyst displayed the highest ethylbenzene conversion and styrene yield, owing to the optimization of active phase content and electron transfer ability. Further, higher  $CeO_2$  content not only enhanced styrene selectivity (as a result, K/Ce-1.12 had the best selectivity), but also prolonged the life cycle of catalysts.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2015.09.027.

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