



Short communication

Optimum ratio of K₂O to CeO₂ in a wet-chemical method prepared catalysts for ethylbenzene dehydrogenationYang Li^a, Yuyang Cui^a, Xiang Zhang^a, Yinghua Lu^a, Weiping Fang^a, Yiquan Yang^{a,b,*}^a College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China^b National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, Xiamen University, Xiamen 361005, China

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ABSTRACT

Fe₂O₃–K₂O–CeO₂ catalysts with various ratios of K₂O to CeO₂ were prepared by the wet-chemical method. Their phase compositions, reducibility, valence states of elements and catalytic activities for ethylbenzene dehydrogenation were studied. The results demonstrated that when the weight ratio of K₂O: CeO₂ 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 CeO₂ content not only enhanced styrene selectivity, 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, Fe₂O₃ 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 CeO₂, could improve the catalytic activities of Fe₂O₃–K₂O based catalysts [5–12]. CeO₂ 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 CeO₂ 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 CeO₂ is described in Fig. S1 (Supporting information) [11,12]. Furthermore, potassium ferrites (e.g., K₂Fe₂₂O₃₄) are the active phases in the catalysts and their transformation states strongly affect the catalytic activities, while CeO₂ facilitates the formation of active phases and stabilize them under reaction conditions at a low water ratio. Moreover,

CeO₂ takes part in the Fe³⁺ + e[−] → Fe²⁺ 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 CeO₂ content leads to better catalytic activity, because Fe₂O₃ and K₂O components are also critical to catalysts (a higher CeO₂ content means a lower content of Fe₂O₃ or K₂O). Therefore, the optimum proportions of them should be discussed.

In our laboratory, we found that when the fraction of Fe₂O₃ 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 K₂O to CeO₂ on the catalysts with fixed contents of Fe₂O₃ and some other metal oxide components. A wet-chemical method was applied to fabricate Fe₂O₃–K₂O–CeO₂ based catalysts. In order to find the optimum K₂O/CeO₂ ratio for EBDH, comprehensive properties of the catalysts, including phase compositions, valence states of elements and catalytic activities, etc., were measured.

2. Experimental

2.1. Catalyst preparation

The catalysts in the present work were composed of Fe₂O₃ (72.15 wt.%), MgO (1.02 wt.%), MoO₃ (1.09 wt.%), K₂O and CeO₂. Notice that except for K₂O and CeO₂, we introduced the promoters of MgO and MoO₃, 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 K₂O and CeO₂ in the catalysts was referred to K/Ce-*x*, where *x* represents the weight ratio of K₂O to CeO₂, 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_2O and CeO_2 in our catalysts. We prepared about 144 g catalysts and the weight of CeO_2 was set to be 13.5, 14.5, 15.5 and 17.5 g. Because the total mass fraction of K_2O and CeO_2 was fixed, we could determine the weight of K_2O and the ratio of K_2O to CeO_2 in each catalyst. The preparation procedures were as follows: (1) Fe_2O_3 powder was mixed with an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ to obtain a metastable suspension; (2) poured the suspension into a mixed solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and K_2CO_3 slowly during stirring; (3) NH_4OH 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 $120^\circ C$ for 4 h and calcined at $250^\circ C$ for 6 h in air to produce a catalyst precursor; (5) mixed the catalyst precursor with sodium carboxymethylcellulose, cement and moderate amount of water to produce a paste, then extruded which to cylindrical strips ($\Phi 3 \times 5$ mm); and (6) the final catalysts were obtained after the stripes were dried at $120^\circ C$ for 4 h and calcined at $850^\circ C$ 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_2 (H_2 -TPR) tests were performed under H_2 /Ar flow (30 ml/min; H_2 volume fraction was 5%) in a temperature range from 50 to $900^\circ C$ with a heating rate of $10^\circ C$ /min. Consumption amount of H_2 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 $610^\circ C$. During the reaction process, a mixture of gas of ethylbenzene (2.5 ml/h) and H_2O (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

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

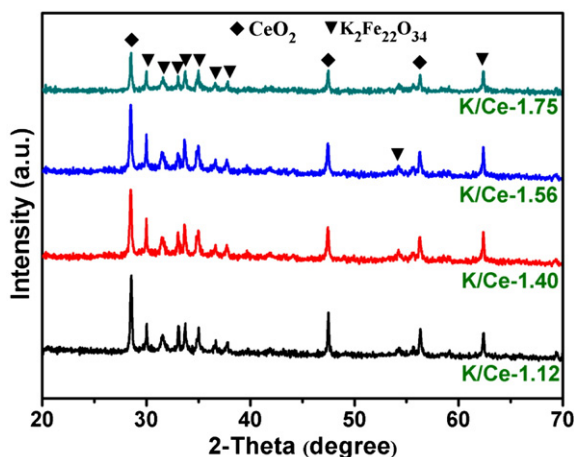


Fig. 1. XRD patterns of the catalysts.

peaks arising from CeO_2 become stronger and sharper with a decreasing weight ratio of K_2O to CeO_2 . Obviously, this can be attributed to the increasing content and grain size of CeO_2 [14]. While for the active phase of $K_2Fe_{22}O_{34}$, 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_2 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 $K_2Fe_{22}O_{34}$ content (K/Ce-1.75 has the lowest CeO_2 loading). Therefore, the K_2O/CeO_2 ratio not only directly decides CeO_2 content in the catalysts, but also affects the amount of active phases.

3.2. H_2 -TPR tests

H_2 -TPR profiles are given in Fig. 2. Several peaks can be observed from each curve. For instance there are two strong peaks at about $450^\circ C$ and $750^\circ C$. They are corresponding to the reduction process of $Fe^{3+} \rightarrow Fe^{2+}$ (low temperature peak) and $Fe^{2+} \rightarrow Fe$ (high temperature peak) [4,6,16]. As a whole, higher CeO_2 content hinders the reducibility of Fe^{3+} (Fe_2O_3) to Fe^{2+} (Fe_3O_4) [10]. Furthermore, two intense hydrogen consumption bands can be observed at about $475^\circ C$ and $780^\circ C$ (the circled zones in Fig. 2). They result from the reduction of surface oxygen and bulk oxygen from CeO_2 ($CeO_2 \rightarrow Ce_2O_3$) [13,17]. Because CeO_2 (Ce^{4+}) and Ce_2O_3 (Ce^{3+}) have similar crystal structures (CaF₂-typed), Ce^{4+} and Ce^{3+} are easy to coexist.

Copresence of Fe^{3+} and Ce^{3+} is possible on the basis of the reduction potential of the $Fe^{2+/3+}$ and $Ce^{3+/4+}$ couples. Significantly, the combined action of Fe^{3+} and Ce^{3+} plays a positive role in EBDH: during EBDH reaction, α -hydrogen of ethylbenzene attacks the acid site of the catalysts (Fe^{3+}) and simultaneously, β -hydrogen attacks the basic site (Ce^{3+}), as shown in Fig. S2 [10,18,19], while positive charge on α -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_2 content is beneficial for the keeping of Fe^{3+} (instead of being reduced to Fe^{2+}) and the coexisting of Fe^{3+} and Ce^{3+} .

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_{5/2} 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^{4+} . 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^{3+} 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.

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