catalysts

MDPI

Article

Supporting Information:

Efficient oxidative dehydrogenation of ethylbenzene over K/CeO_2 with exceptional styrene yield

He Sun, Juping Zhang, Kongzhai Li, Hua Wang and Xing Zhu*

State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China
*Corresponding author: zhuxing2010@hotmail.com

This document provides additional information on experimental details, redox catalyst characterizations and reactivity data.

Table S1. Enthalpy change of reaction at different temperatures.

Temperature (℃)	C_8H_{10}(EBZg)+CO_2(g)=C_8H_8(STYg)+CO(g)+H_2O(g) deltaH (kJ)	C_8H_{10}(EBZg)+0.5O_2(g)=C_8H_8(STYg)+H_2O(g) deltaH (kJ)
300	161.512	-122.119
350	161.589	-122.003
400	161.608	-121.916
450	161.571	-121.858
500	161.478	-121.836
550	161.325	-121.856
600	161.108	-121.925
650	160.819	-122.054

The reaction equations of ethylbenzene with CO_2 and ethylbenzene with O_2 were imported into the HSC simulation software, and the temperature range of the simulation experiments was set to 300-700°C, and the information was collected at 50°C intervals. The values of enthalpy changes of the reactions at different temperatures obtained were collected and organized as shown in Table S1.

TableS2. Thermoneutral reaction equation.

Temperature (℃)	$\mathbf{X}C_8H_{10}(g)+CO_2(g)+\mathbf{Y}O_2(g)=\mathbf{X}C_8H_8(g)+CO(g)+\mathbf{X}H_2O(g)$
300	$2.3226C_8H_{10}(g)+CO_2(g)+0.6613O_2(g)=2.3226C_8H_8(Yg)+CO(g)+2.3226H_2O(g)$
350	$2.3245C_8H_{10}(g)+CO_2(g)+0.6622O_2(g)=2.3245C_8H_8(Yg)+CO(g)+2.3245H_2O(g)$
400	$2.3256C_8H_{10}(g)+CO_2(g)+0.6628O_2(g)=2.3256C_8H_8(Yg)+CO(g)+2.3256H_2O(g)$
450	$2.3259C_8H_{10}(g)+CO_2(g)+0.6629O_2(g)=2.3259C_8H_8(Yg)+CO(g)+2.3259H_2O(g)$
500	$2.3254C_8H_{10}(g)+CO_2(g)+0.6627O_2(g)=2.3254C_8H_8(Yg)+CO(g)+2.3254H_2O(g)$
550	$2.3239C_8H_{10}(g)+CO_2(g)+0.6619O_2(g)=2.3239C_8H_8(Yg)+CO(g)+2.3239H_2O(g)$
600	$2.3214C_8H_{10}(g)+CO_2(g)+0.6607O_2(g)=2.3214C_8H_8(Yg)+CO(g)+2.3214H_2O(g)$
650	$2.3176C_8H_{10}(g)+CO_2(g)+0.6588O_2(g)=2.3176C_8H_8(Yg)+CO(g)+2.3176H_2O(g)$

Figure 3.1 was plotted based on Table S1, and it was found that the reaction enthalpy changes of both reactions were in the same order of magnitude. After coupling the enthalpy changes of the two reactions to zero, the equation coefficients were changed and collated and recorded as Table 1. The equation coefficients of EB, CO_2 and O_2 at different temperatures were filled into the equations in Table 1, and the thermoneutral reaction equations at different temperatures as well as mixed atmosphere conditions were obtained and collated as shown in Table S2.

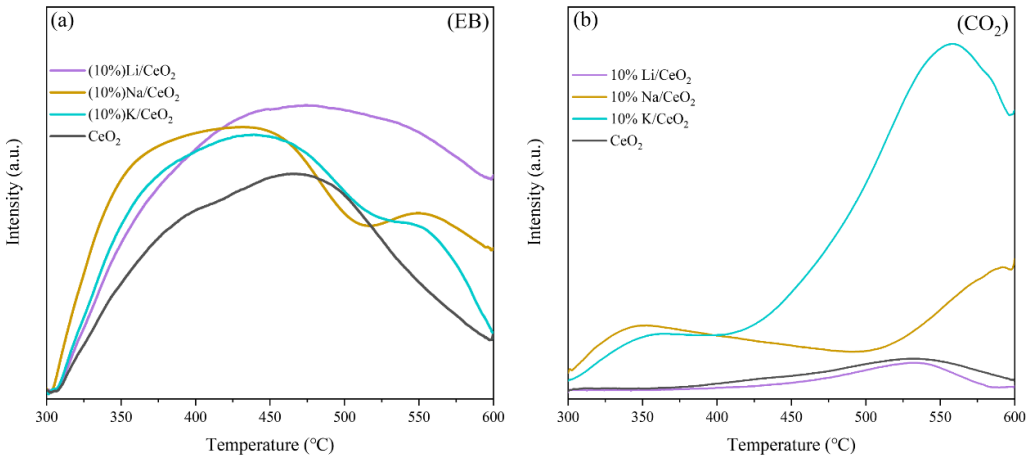

Figure S1. EB-temperature program reduction. (a) ethylbenzene (EB); (b) H_2O. reaction conditions: ramp rate 10 °C/min, T_{EB} = 25 °C, space velocity = 7.5 h^{-1}, 10%X/CeO_2 (X=Li, Na, K).

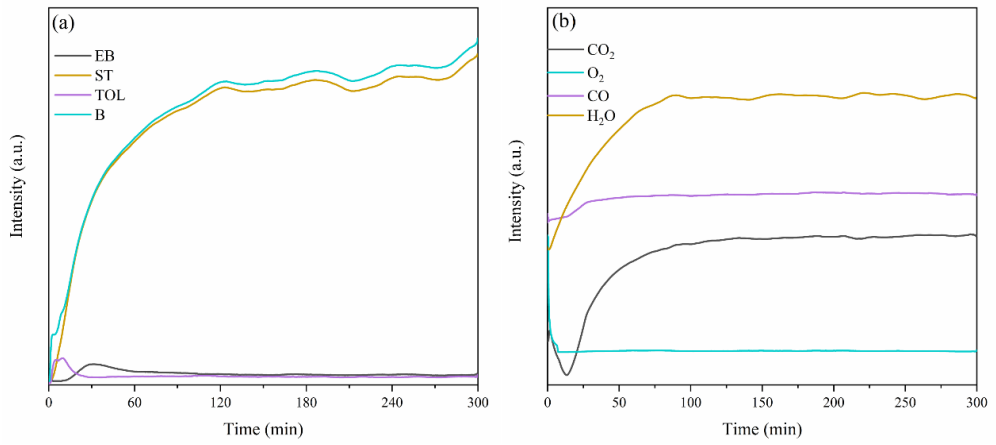

Figure S2. Mass spectra of (**a**) reactants and (**b**) products of EB-ODH under mixed atmosphere of CO_2-4O_2. Experimental conditions: reaction temperature 500 ℃, TEB=25 °C, reaction time 5 h, flow rate 25 mL/min, atmosphere CO_2-O_2/Ar, catalyst dosage 1000 mg, space velocity =5.0 h^{-1}.

Raman characterization of the catalyst surface structure changes before and after the 50h stability test. As shown in Figure S3, Raman characterization of the catalyst surface structure changes before and after the 50 h stability test. The band at 477 cm^{-1} can be assigned to F_{2g} vibration mode of the fluorite structure (Fm3m space group), corre-sponding to the symmetrical stretching mode of Ce-O bonds[1]. The sample 10% K/CeO_2 after stability testing showed a small amount of carbon accumulation at 1330 and 1600 cm^{-1}. The presence of a small amount of carbon accumulation did not affect the performance of the catalyst[2].

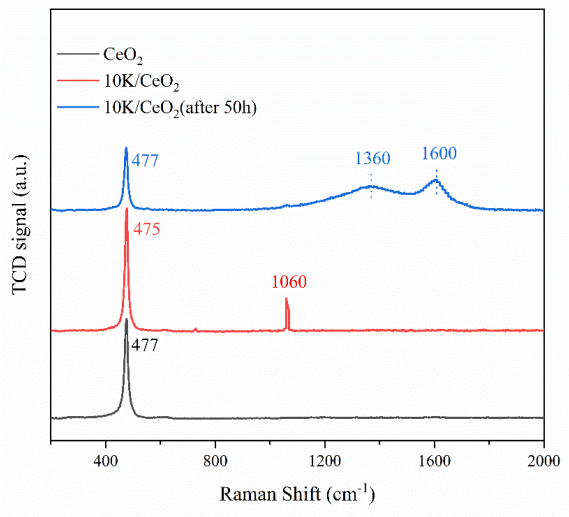

Figure S3. Raman of samples before and after stability testing of 10% K/CeO_2.

References

[1] Wang Huan, Cao Fang-Xian, Song Yong-Hong, Yang Guo-Qing, Ge Han-Qing, Liu Zhao-Tie, Qu Yong-Quan, Liu Zhong-Wen. Two-step hydrothermally synthesized $Ce_{1-x}Zr_xO_2$ for oxidative dehydrogenation of ethylbenzene with carbon dioxide [J]. Journal of CO_2 Utilization, 2019, 34: 99-107.

[2] Zhang Li, Wu Zili, Nelson Nicholas C., Sadow Aaron D., Slowing Igor I., Overbury Steven H. Role Of CO_2 As a Soft Oxidant For Dehydrogenation of Ethylbenzene to Styrene over a High-Surface-Area Ceria Catalyst [J]. ACS Catalysis, 2015, 5(11): 6426-35.