Supporting information for

Mesoporous $x\mathrm{Er_2O_3{\cdot}CoTiO_3}$ Composite Oxide Catalysts for Low Temperature Dehydrogenation of Ethylbenzene to Styrene by Using CO_2 as a Soft Oxidant

Yanfeng Yue,[a,b] **Li Zhang,**[a] **Jihua Chen,**[c] **Dale K. Hensley,**[c] **Sheng Dai**[a,d,*] **and Steven H. Overbury**[a,*]

[a]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
[b]Department of Biology, Geology, and Physical Science, Sul Ross State University, Alpine, Texas 79832, USA
[c]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
[d]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA

Containing the following details:

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2. Powder XRD patterns of metal oxides prepared from with different molar ratio
3. Powder XRD patterns of metal oxides prepared from sole metal salt precursor
4. Powder XRD patterns of $0.5\mathrm{Er_2O_3{\cdot}CoTiO_3}$-*T*
5. Elemental analysis of the typical $0.25\mathrm{Er_2O_3{\cdot}CoTiO_3}$-*600*
6. Porosity measurements of $0.5\mathrm{Er_2O_3{\cdot}CoTiO_3}$ prepared under different calcination temperature
7. Porosity measurements of metal oxides
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1. Experimental and characterizations

1.1 Experimental details

1.1.1 Materials

Pluronic P123 (M_{av} = 5800, $EO_{20}PO_{70}EO_{20}$), Titanium(IV) iso-propoxide (97%, Mw = 284), Erbium(III) nitrate pentahydrate (99.9%, Mw = 443), and Cobalt(II) nitrate hexahydrate (98%, Mw = 291) were purchased from from Aldrich and used without further purification.

1.1.2 Synthesis of Metal Oxides

This series of composite metal oxides was prepared following a literature method.[1] The purchased metal salts and template agent (Pluronic P123, 1.0 g) were dissolved in 15 mL ethanol in required stoichiometric proportions. The mixed solutions were then stirred in a magnetic blender at room temperature. After 2 hrs, the suspension was aged on a hot plate at 40°C for 24 hrs and dried at 100 °C for another 24 hrs to obtain the precursor samples. Then, the resulting powders were finally calcined under desired temperature (800, 700, and 600 °C) for 6 hrs. In a typical synthesis of $0.25Er_2O_3{\cdot}CoTiO_{34}$-*600*, 1.0 g of Pluronic P123was dissolved in 15 mL of ethanol at room temperature. 1.11g Erbium(III) nitrate pentahydrate, 2.93g Titanium iso-propoxide, and 2.97g Cobalt nitrate hexahydrate were added into the above solution with vigorous stirring. After stirring at room temperature for about 2 hrs, and the resulting suspension was aged on a hot plate at 40°C for 24 hrs and dried at 100 °C for another 24 hrs to obtain the brown precursor sample. Calcination of the precursor sample was carried out by slowly increasing temperature from room temperature to 600 °C (1 °C min^{-1} ramping rate) and by heating at 600 °C for 6 hrs in air. This series of metal oxides were labeled as $xEr_2O_3{\cdot}CoTiO_{34}$-$T$, in which x stands for molar ration of element Er to Ti and Co, and T stands for the calcination temperature in °C.

1.2 Characterizations

1.2.1 Powder X-ray Diffraction (XRD). Powder X-ray Diffraction (XRD) analysis of the $xEr_2O_3{\cdot}CoTiO_{34}$-$T$ series was used to confirm the crystallinity as well as the phase purity of the bulk materials. Powder XRD patterns were recorded on a PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å).

1.2.2 Scanning Electron Microscopy (SEM). Samples for SEM analysis were prepared by drop casting: one drop of the sample dispersion in ethanol was dropped onto a copper grid and allowed to dry at ambient temperature before being subjected to SEM analysis. The scanning electron microscope images were obtained in a Carl Zeiss Merlin SEM operating at 1.7 kV for imaging and 15 kV for the EDS. The energy-dispersive X-ray spectroscopy (EDX) results were obtained with a system from Bruker Nano GmbH using an XFlash detector 5030.

1.2.3 Transmission Electron Microscopy (TEM). Samples for TEM analysis were prepared by drop casting: one drop of the sample dispersion in ethanol was dropped onto a copper grid and allowed to dry at ambient temperature before being subjected to TEM analysis. Electron diffraction and TEM experiments were examined with a Zeiss Libra 120 at 120 kV. An emission current as low as 5μA and minimal exposure times were used to effectively reduce electron-beam-induced sample damage, along with frequent morphology monitoring. Selected area electron diffraction experiments used an aperture size of about 1 micron in diameter and the obtained diffraction patterns were calibrated against thin film gold standard, assuming the d spacing of Au (111) planes is 0.235 nm.

1.2.4 Gas Adsorption Analysis. Gas adsorption studies were done to confirm the permanent porosity of the as-made metal oxides, as well as to determine the surface area. Gas adsorption experiments were performed on a Micromeritics Tristar 3000 at 77 K. Samples (around 100 mg) were activated for 6 hours at 110 °C under nitrogen flow and subsequently loaded for adsorption analysis.

1.2.5 Catalytic Test (ODH). 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 CO_2 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 programmable temperature controller of an Zeton Altamira (AMI-200) instrument. The dehydrogenation catalyst (200 mg, 60–80 mesh) was mixed with 200 mg of quartz beads with the similar size and filled into the reactor and pretreated for 1 hr at 400 °C with 5 % O_2/Ar gas prior to performing a reaction. The liquid ethylbenzene was supplied by means of a motorized syringe pump (New era pump system, NE1000). Ethylbenzene as a reactant (2.204 µmol/min), CO_2 (5 mL/min), Ar as a carrier (15 mL/min), and total flow rate of 20 mL/min. The reactants and products were analyzed using a continuously sampling mass spectrometer (Pfeiffer-Balzers Instruments) followed by a gas chromatograph (Buck) equipped with a flame ionization detector. For analysis of the products, HP-innowax 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 H_2, CO, and CO_2 were monitored by the mass spectrometer. The total carbon balance closed to within ± 5%.

Reference

[1] Q. Yuan, A.-X. Yin, C. Luo, L.-D. Sun, Y.-W. Zhang, W.-T. Duan, H.-C. Liu, C.-H. Yan, *J. Am. Chem. Soc.*, **2008**, *130*, 3465–3472.

2. PXRD patterns of metal oxides prepared from with different molar ratio

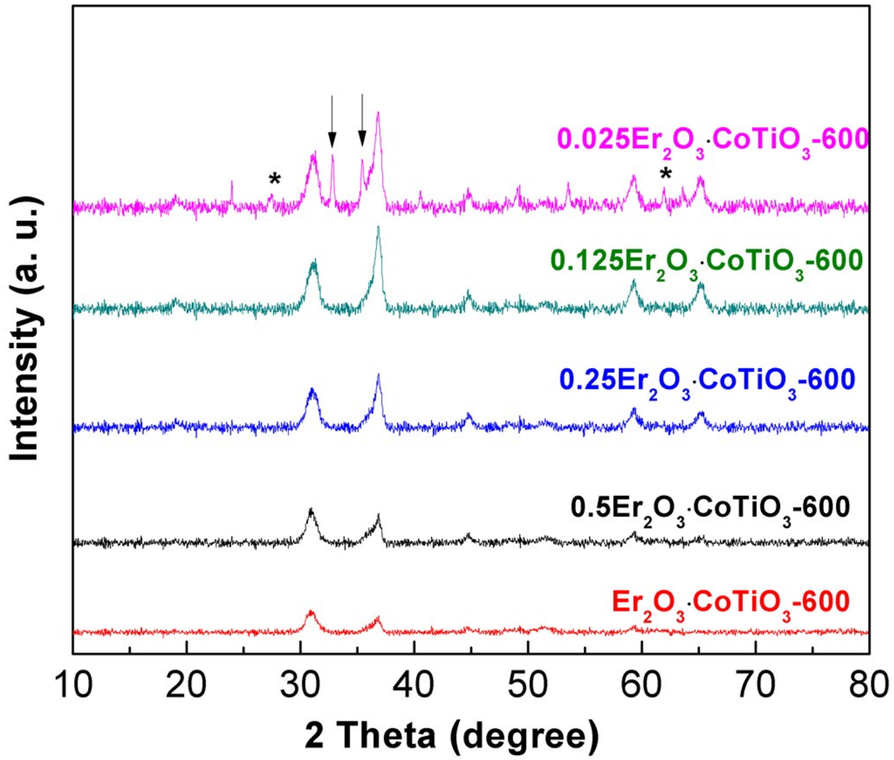


Figure S1. XRD patterns of as made *x*Er$_2$O$_3$·CoTiO$_{34}$-*600* series have a main phase of CoTiO$_3$ (ICSD 01-077-1373),[2] with asterisks and arrows refer to TiO$_2$ and Co$_3$O$_4$ impurities when the molar ratio of Er, Ti, and Co reached to 1:40:40.

Reference

[2] K. Kidoh, K. Tanaka, F. Marumo, H., Takei *Acta Crystallogr., Sec. B: Struct. Sci*., **1984**, *40*, 92.

3. PXRD patterns of metal oxides prepared from sole metal salt precursor

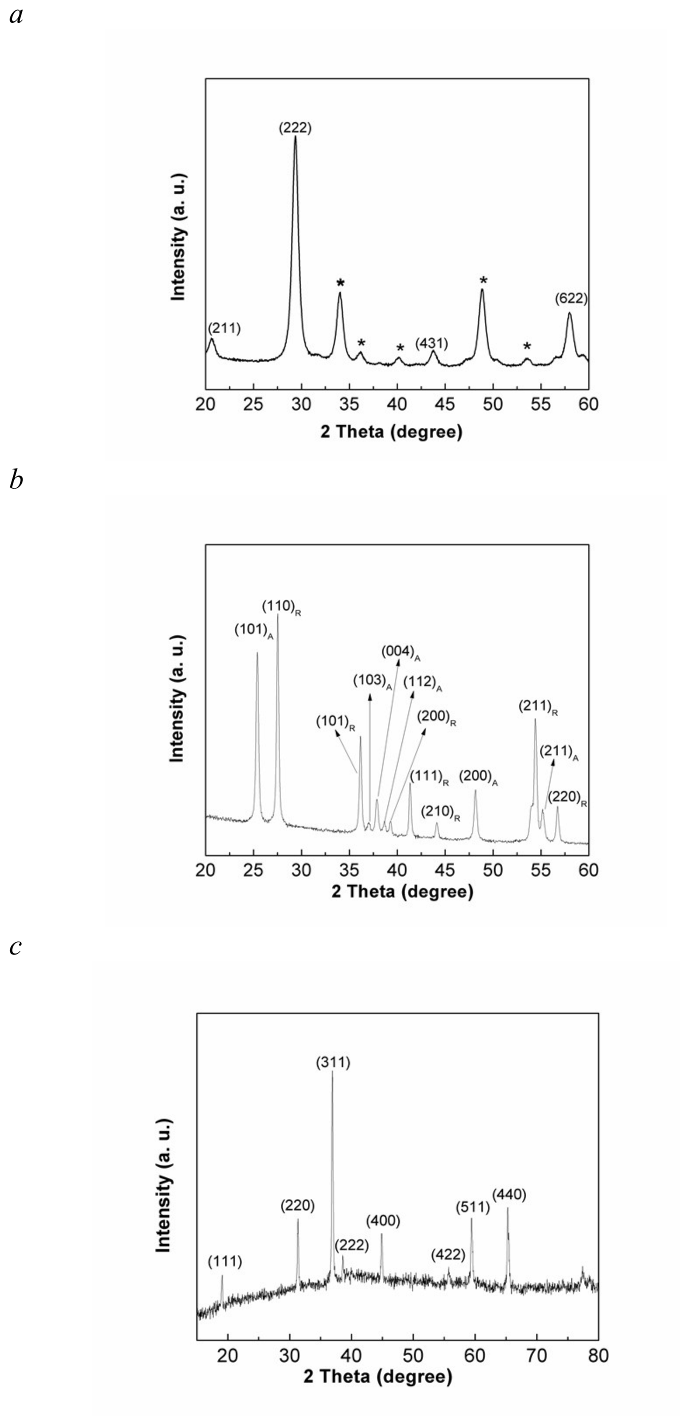


Figure S2. XRD patterns of Er_2O_3-600 with asterisks refer to a new phase different from the cubic structure of Er_2O_3 (*a*), mixed rutile and anatase TiO_2-600 (*b*) and Co_3O_4-600 (*c*).

4. PXRD patterns of *0.5*Er_2O_3·$CoTiO_{34}$-*T*

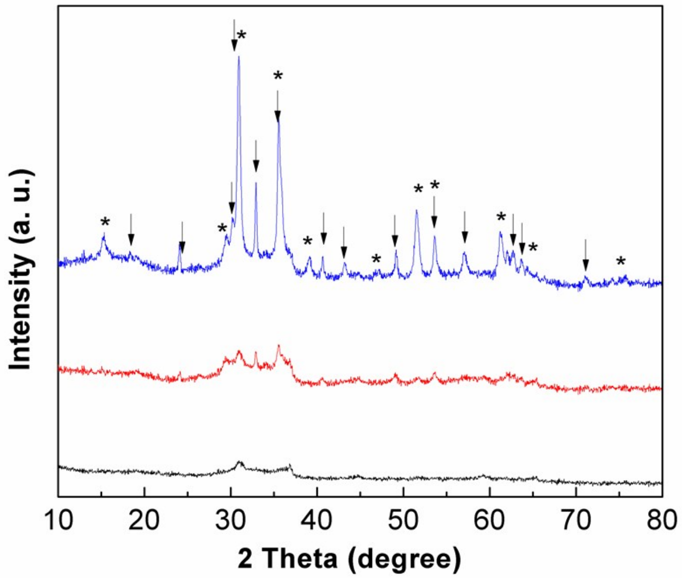


Figure S3. XRD patterns of *0.5*Er_2O_3·$CoTiO_{34}$-*600* (black), *0.5*Er_2O_3·$CoTiO_{34}$-*700* (red) and 0.*5*Er_2O_3·$CoTiO_{34}$-*800* (blue). For 0.*5*Er_2O_3·$CoTiO_{34}$-*800*, asterisks and arrows refer to $Er_2Ti_2O_7$ (ICSD 00-055-0813) and $CoTiO_3$ (ICSD 01-077-1373), respectively.

5. Elemental analysis of the typical *0.5*$Er_2O_3\cdot CoTiO_3$-*600*

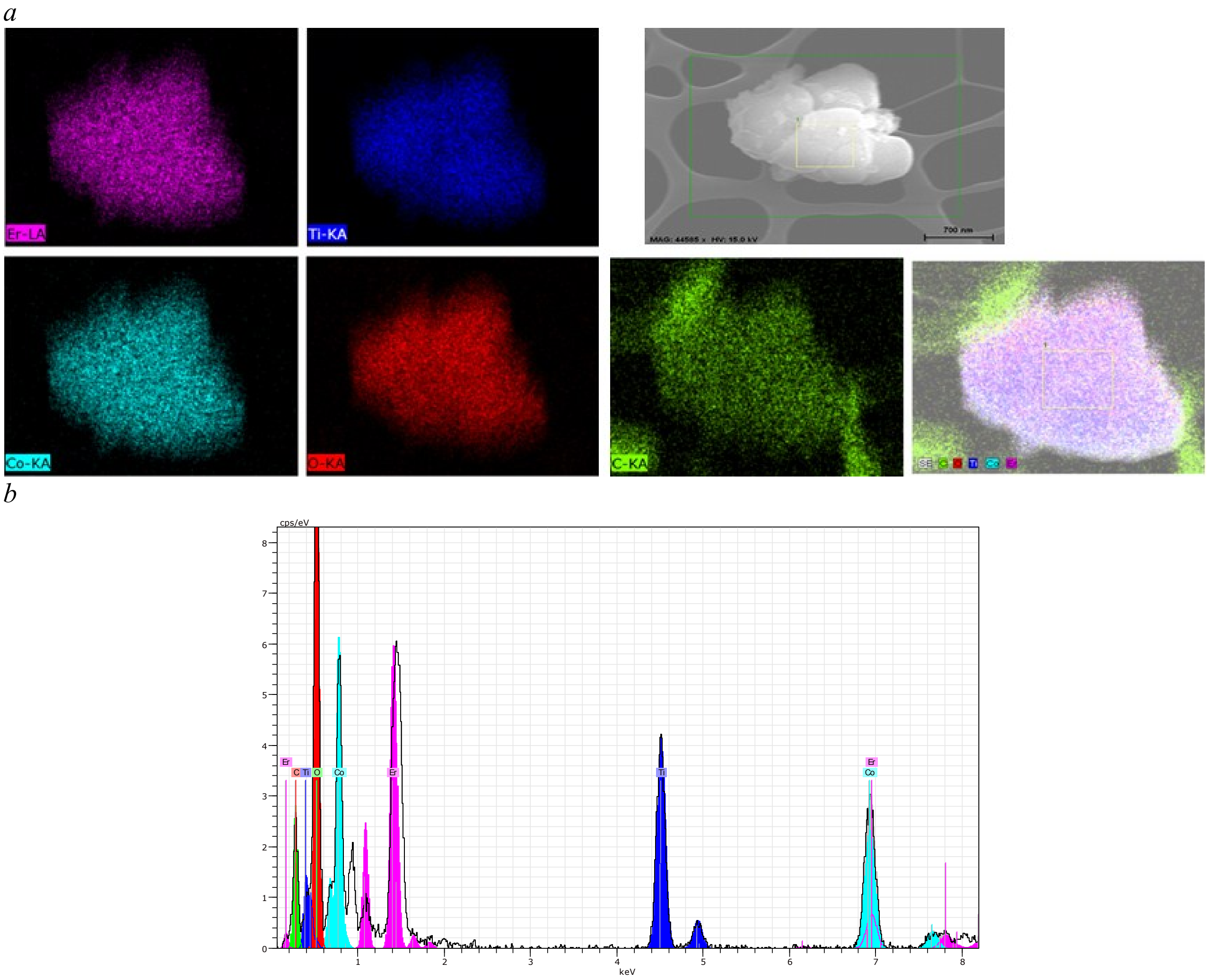
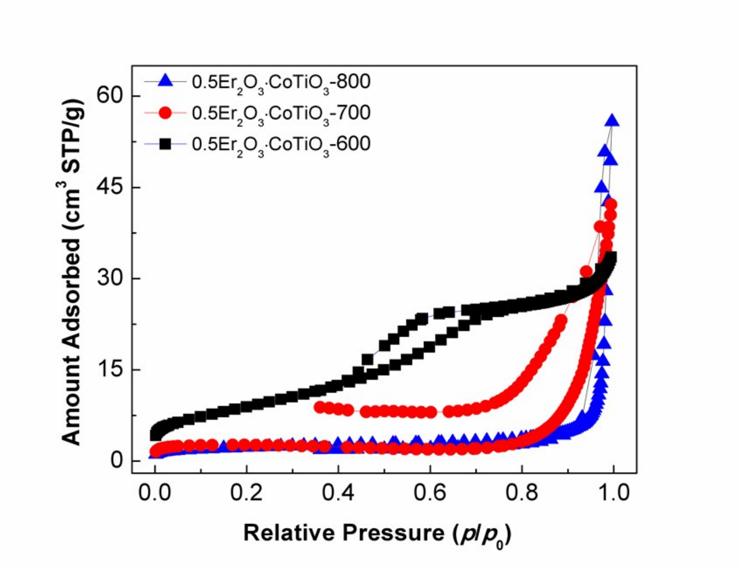


Figure S4. EDS elemental maps showing the spatial distribution of Er, Ti, Co, O, and C in of typical mesoporous *0.5*$Er_2O_3\cdot CoTiO_3$-*600* material (*a*), and related EDAX analysis (the wt% being 19.04, 19.04, and 28.12 % and the related molar ratio being 1: 3.54: 4.19 for Er, Ti and Co elements) (*b*).

6. Porosity measurements of *0.5*$Er_2O_3 \cdot CoTiO_3$-*T* prepared under different calcination temperature

a



b

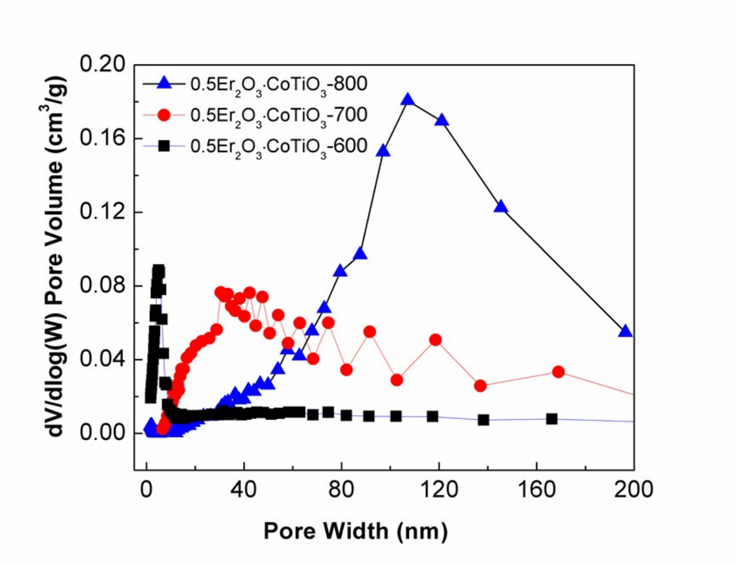
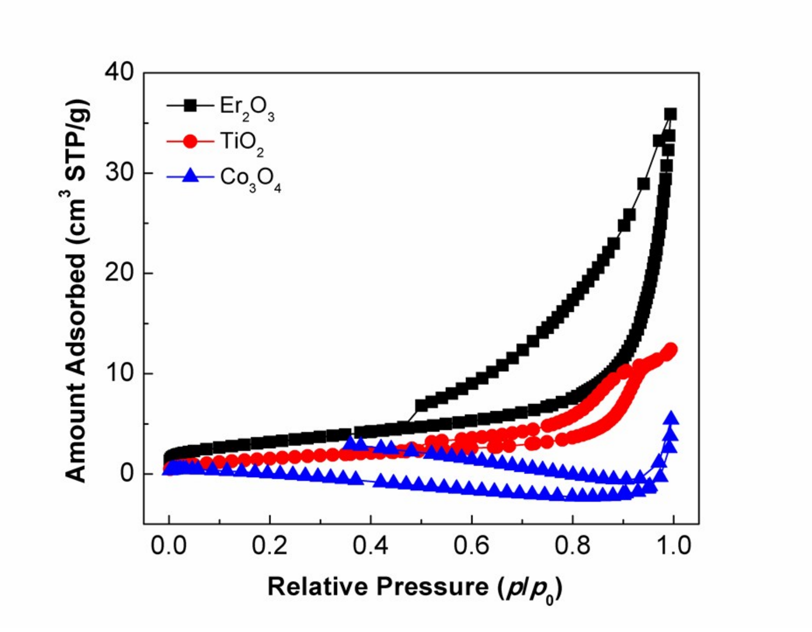


Figure S5. N_2 adsorption-desorption isotherms (*a*) and pore size distribution curves (*b*) of *0.5*$Er_2O_3 \cdot CoTiO_3$-*T* metal oxides obtained under different calcination temperature.

7. Porosity measurements of metal oxides

a



b

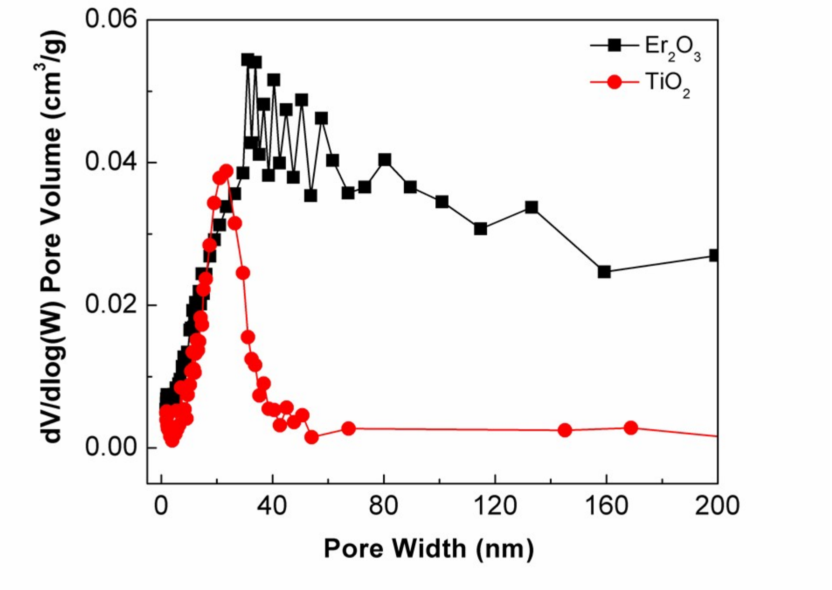


Figure S6. N_2 adsorption-desorption isotherms (*a*) and pore size distribution curves (*b*) of Er_2O_3, TiO_2, and Co_3O_4. Due to the very low N_2 uptake, no pore size distribution curve for the Co_3O_4 was obtained.

8. Plot of the styrene production rate vs surface area

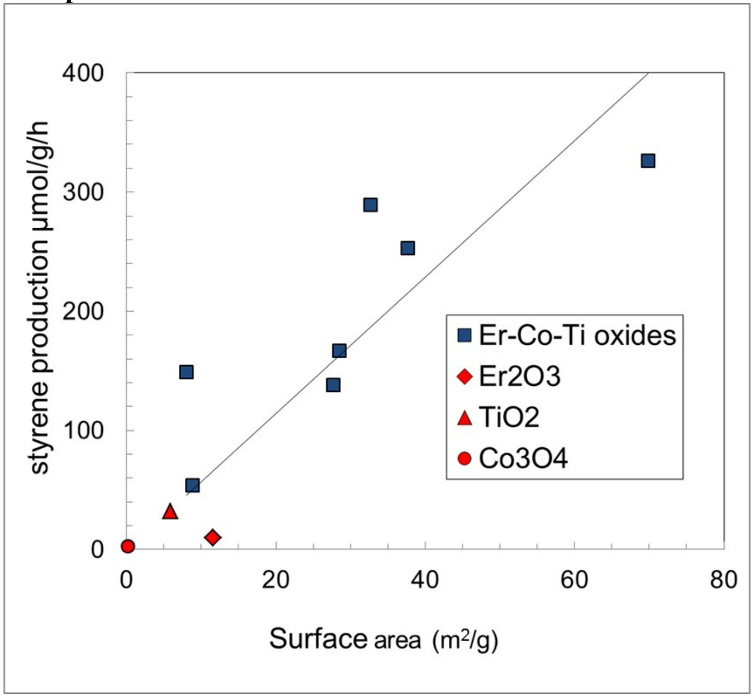


Figure S7. Plot of the styrene production rate vs surface area at 450 °C over different composite metal oxides.