

Electronic Supplementary Information for

**Mesoporous strong base supported cobalt oxide as the  
catalyst for the oxidation of ethylbenzene**

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## Experiment

### Synthesis of SBA-15

Mesoporous silica SBA-15 was synthesized according to the reported method. Pluronic P123 (4.02 g) was added to a solution of HCl (2 M, 100 mL) and distilled water (30 g) at 313 K. Then, tetraethoxysilane (8.32 g) was added in and stirred for 24 h. The resulting mixture was then transferred into a teflon-lined autoclave and heated at 393 K for 72 h. The solid material was filtered and washed with ethanol by a Soxhlet apparatus to remove the surfactant. The final material was dried at 353 K.

### Synthesis of ZrSBA-15

ZrO<sub>2</sub> was introduced to SBA-15 by ammonia/water-induced hydrolysis (AIH) method. The ZrO(NO<sub>3</sub>)<sub>2</sub> was dissolved in deionized water, followed by the addition of SBA-15 under stirring for 24 h. The mixture was evaporated at 353 K followed by drying at 373 K for 4 h. The precursor-loaded SBA-15 was put in an open vial and kept inside an autoclave containing NH<sub>3</sub>-H<sub>2</sub>O solution (50%) without direct contact between the solid and solution. The tightly closed autoclave was then heated to 333 K for 0.5 h. Finally, the solid was dried at room temperature for 6 h and then at 373 K for 12 h, and calcined at 773 K for 5 h under air.

### Synthesis of Co-KZrSBA-15 and Co-ZrSBA-15

The cobalt oxide and potassium were introduced by wet impregnation. Typically, 50 mg of KNO<sub>3</sub> and 30 mg Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 5 mL of deionized water, followed by the addition of 200 mg of ZrSBA-15. After stirring at room temperature for 24 h, the mixture was evaporated at 353 K and subsequently dried at 373 K for 4 h. The obtained solid was calcined at 823 K. For the non-base site introduced material, the procedure was the same as mentioned above except no KNO<sub>3</sub> was added.

### Characterization of the catalysts

The X-ray powder diffraction (XRD) patterns were obtained using PANalytical X'Pert Pro X-ray Diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.1542$  nm). N<sub>2</sub> physical adsorption-desorption measurement was carried out at 77 K on an Autosorb-1 Quantachrome instrument. Samples were pre-degassed at 393 K for about 10 h to remove water and other physically adsorbed species. Fourier transform infrared (FT-IR) spectra were collected on a Bruker Tensor 27 FT-IR spectrometer in KBr media. Microstructure of the materials were examined by transmission electron microscopy (TEM, JEOL JEM-2000EX). HR-TEM were collected on JEM-2100. scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) were collected on JSM-7800F. CO<sub>2</sub> TPD were collected on Micromeritics AutoChem II.

### Catalytic oxidation of hydrocarbon

Catalytic reactions were performed in a 50 mL of autoclave reactor with a teflon insert inside. Typically, 10 g of ethylbenzene and 20 mg of catalyst were placed in the reactor. Then, after being sealed, the reactor was heated to the reaction temperature, while agitation was ensured by an external magnetic stirrer. Upon heating to the reaction temperature, the reactor was charged with 1.0 MPa of O<sub>2</sub> and O<sub>2</sub> was fed continuously to maintain constant pressure. The reaction was carried out at 393 K for 6 h. Reaction products were identified by Agilent 6890N GC/5973 MS detector and quantitated with an internal standard (1,4-dichlorobenzene) method by Agilent 6890D GC equipped with Innovex capillary column (50 m  $\times$  0.32 mm  $\times$  0.4  $\mu$ m). The products were quantified via a double injection: triphenylphosphine (1 M in THF) was added to one of the samples to reduce the peroxide product to the alcohol. For the kinetic study, Liquid samples (~20  $\mu$ l) were extracted periodically using the syringe. Typically, 8-15 points were used.

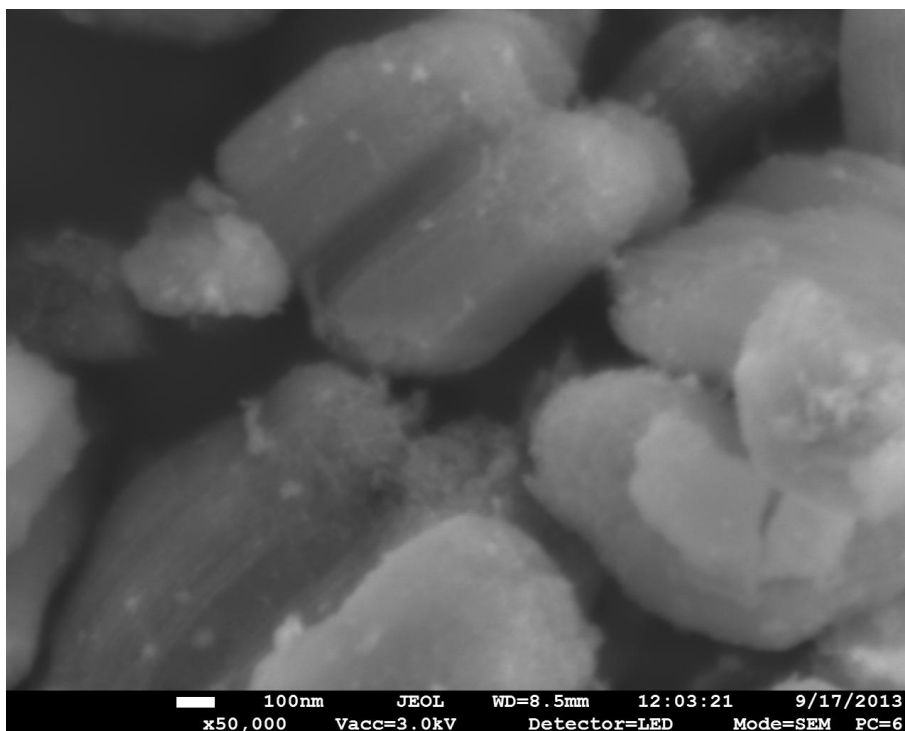


Fig. S1 SEM image of Co-ZrSBA-15

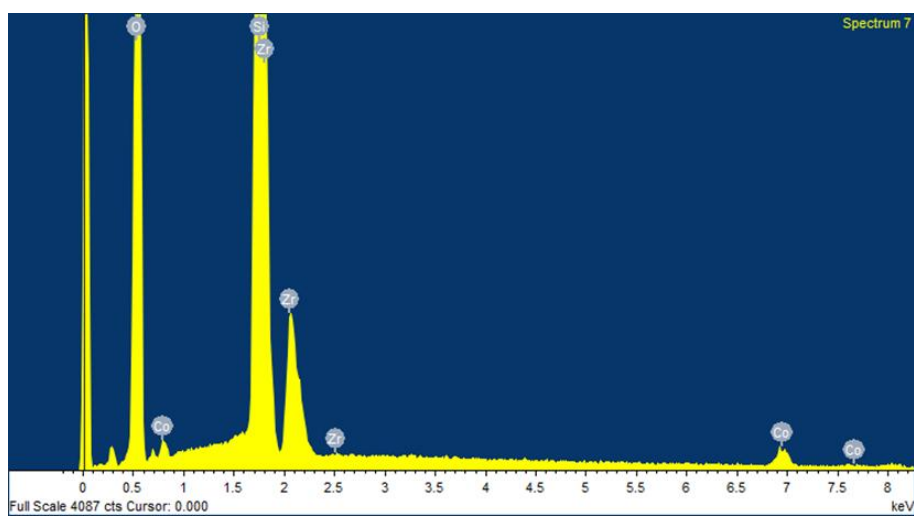


Fig. S2 EDS spectrum of Co-ZrSBA-15

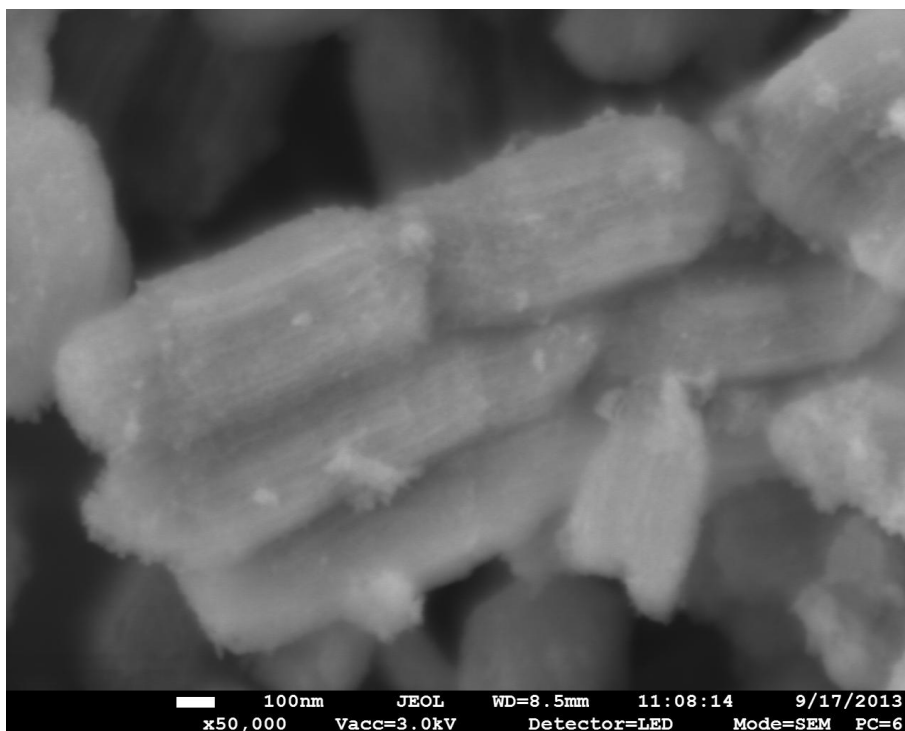


Fig. S3 SEM image of Co-KZrSBA-15

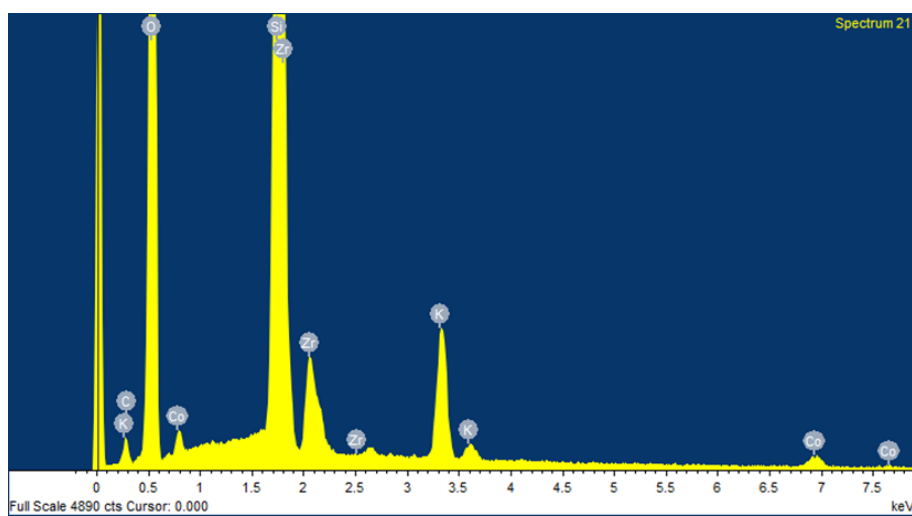


Fig S4 EDS spectrum of Co-KZrSBA-15

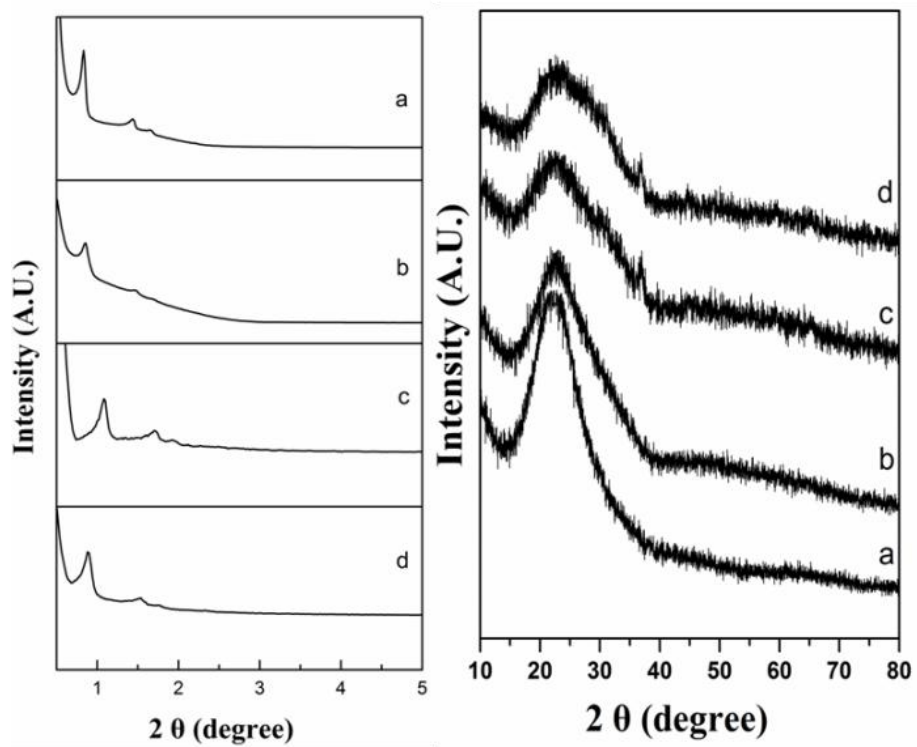


Fig.S5 XRD of the a) SBA-15; b) ZrSBA-15; c) Co-ZrSBA-15; d) Co-KZrSBA-15

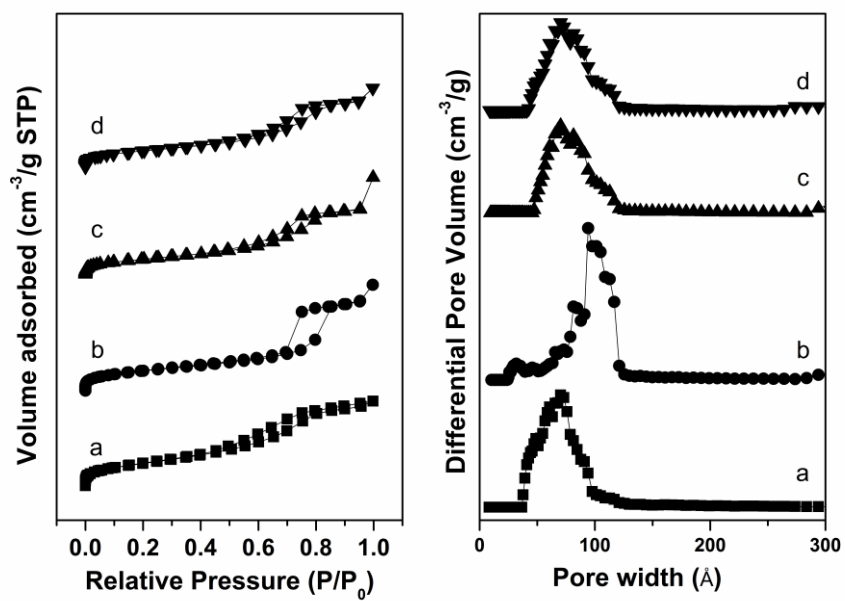


Fig. S6 N<sub>2</sub> adsorption/desorption isotherm and pore size distribution of the a) SBA-15; b) ZrSBA-15; c) Co-ZrSBA-15; d) Co-KZrSBA-15

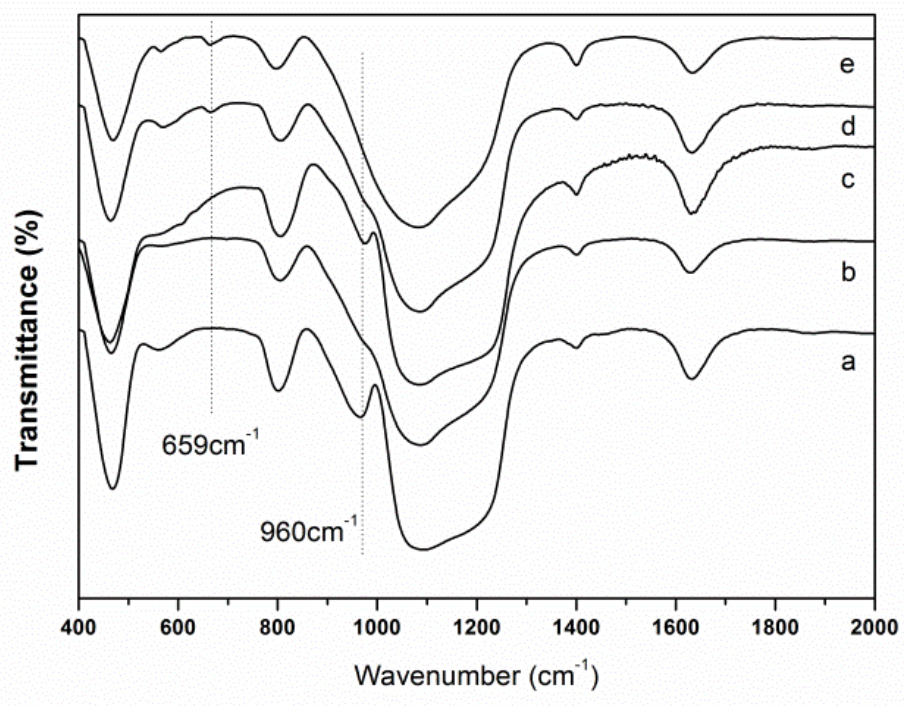


Fig. S7 FT-IR spectra of the a) SBA-15; b) ZrSBA-15; c) SBA-15 calcined at 823 K; d) Co-ZrSBA-15; e) Co-KZrSBA-15

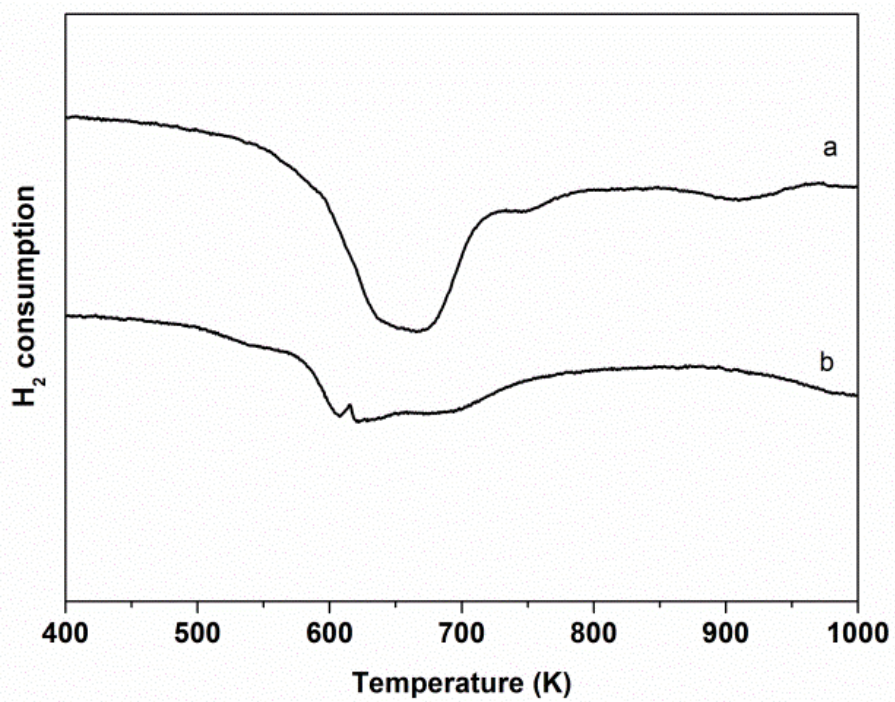


Fig. S8 H<sub>2</sub>-TPR spectra of the a) Co-ZrSBA-15; b) Co-KZrSBA-15



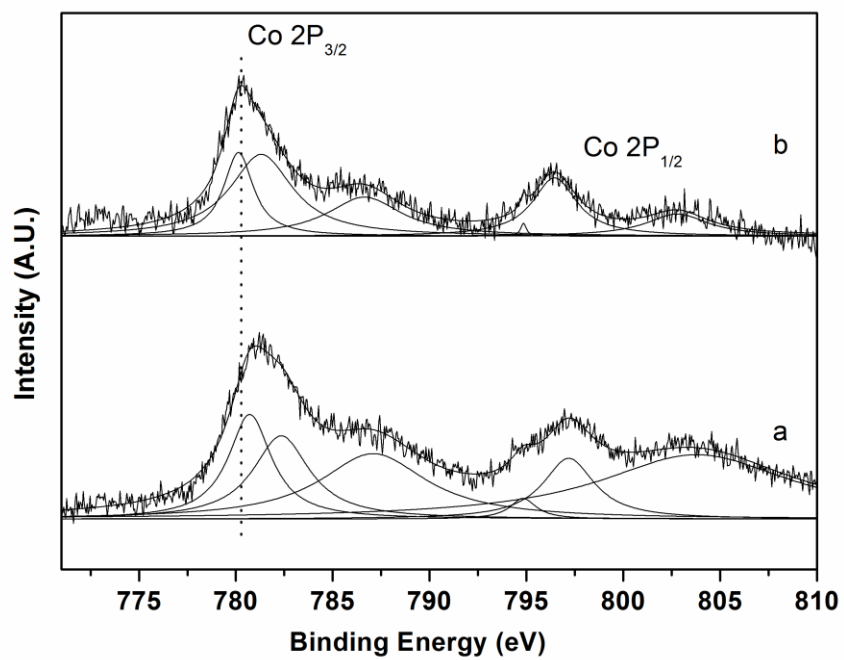


Fig. S9 Co XPS spectra of a) Co-ZrSBA-15; b) Co-KZrSBA-15

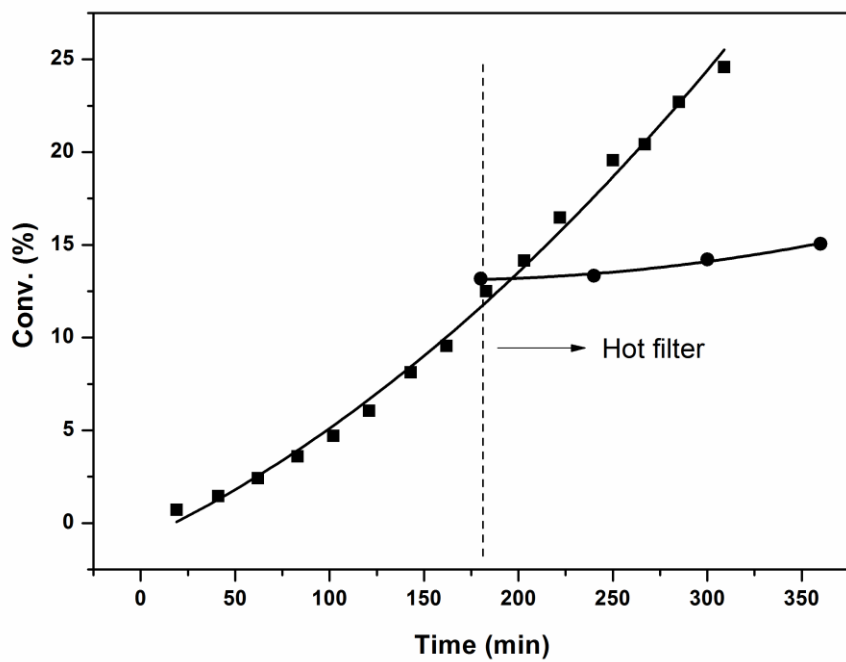


Fig. S10 Conversion of ethylbenzene with Co-KZrSBA-15 and after Co-ZrKSBA-15 removal (at the vertical line).

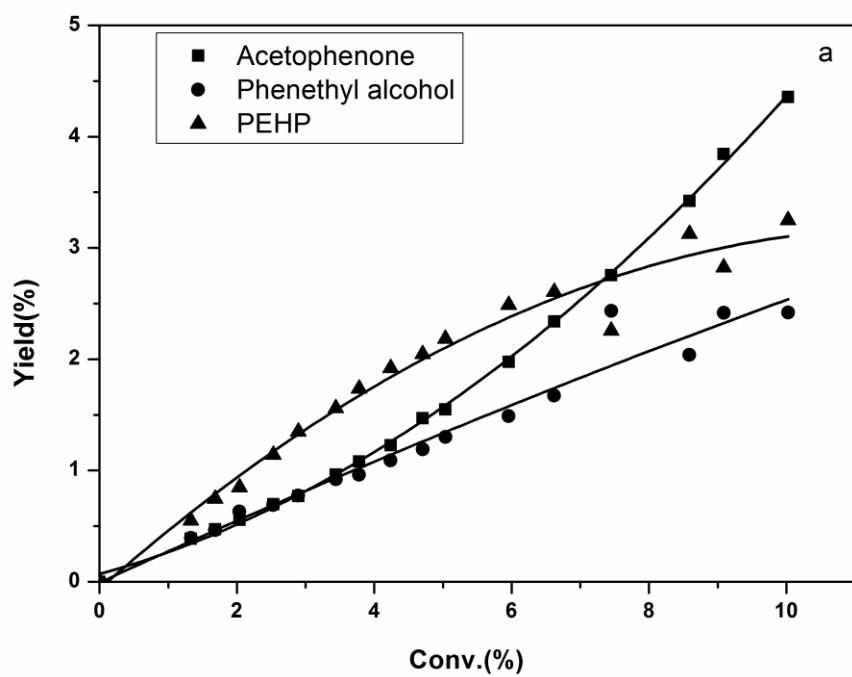
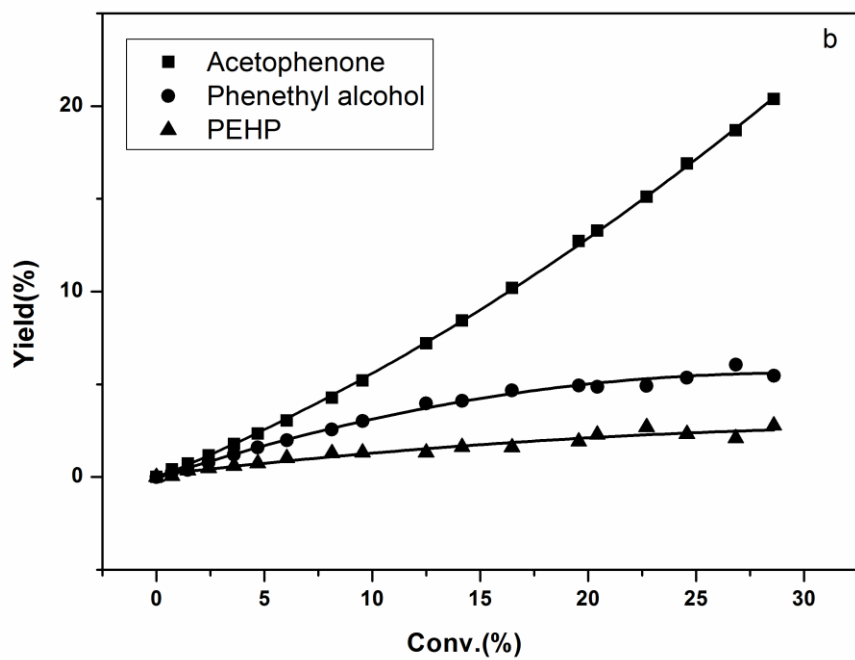
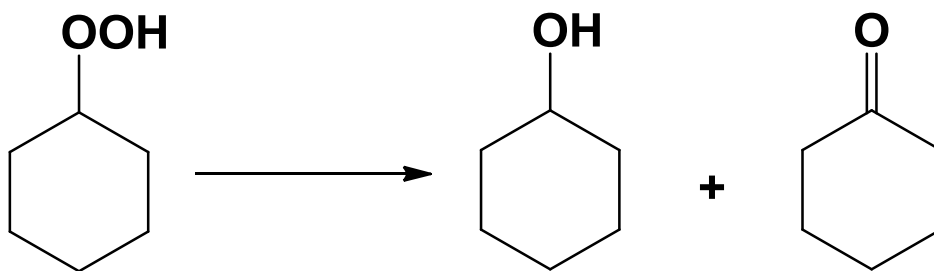


Fig. S11 Product distribution during the reaction process catalyzed by a) Co-ZrSBA-15; b) Co-KZrSBA-15



**Table S1** Decomposition of CHHP over the obtained catalyst

Catalyst	Conv.(%)	Product distribution		
		R=O(%)	R-OH(%)	Others(%)
Co-KZrSBA-15	92.4	31.7	50.6	17.7
Co-ZrSBA-15	46.7	34.3	47.6	18.1

Condition: 5 mL CHHP, 373 K, 10 mg catalyst, 30 min,

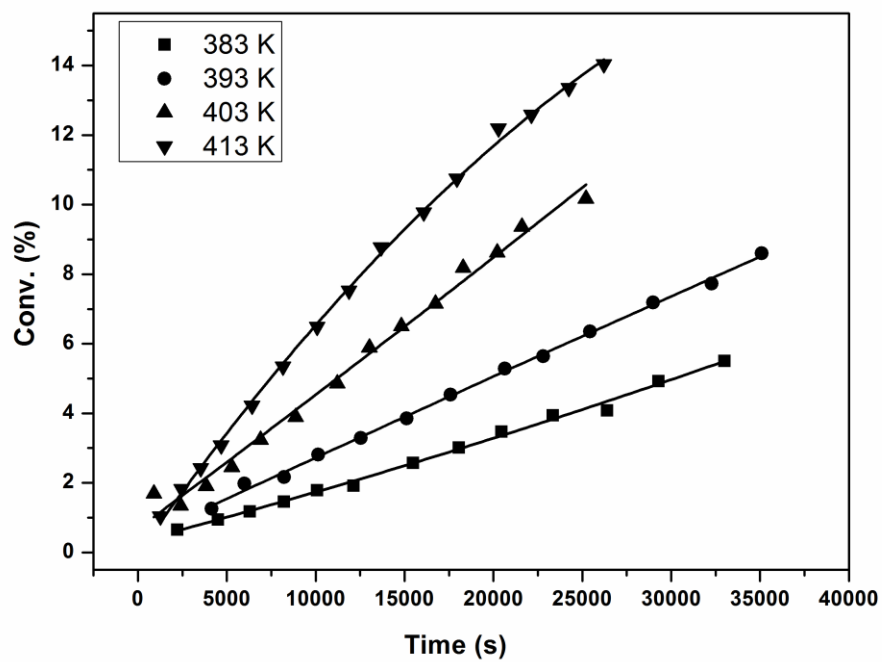


Fig S12 Reaction kinetics of Co-ZrSBA-15

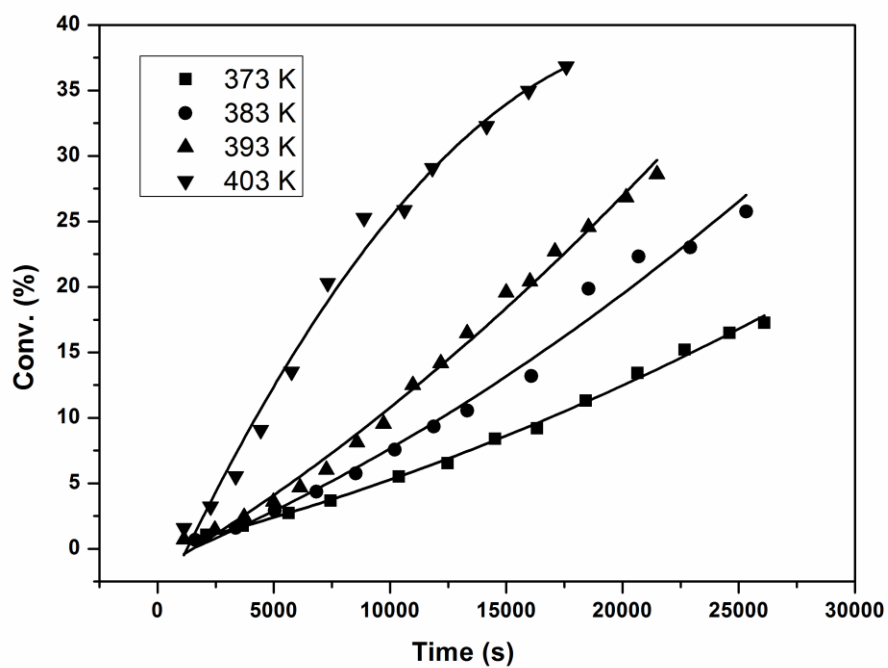


Fig S13 Reaction kinetics of Co-KZrSBA-15

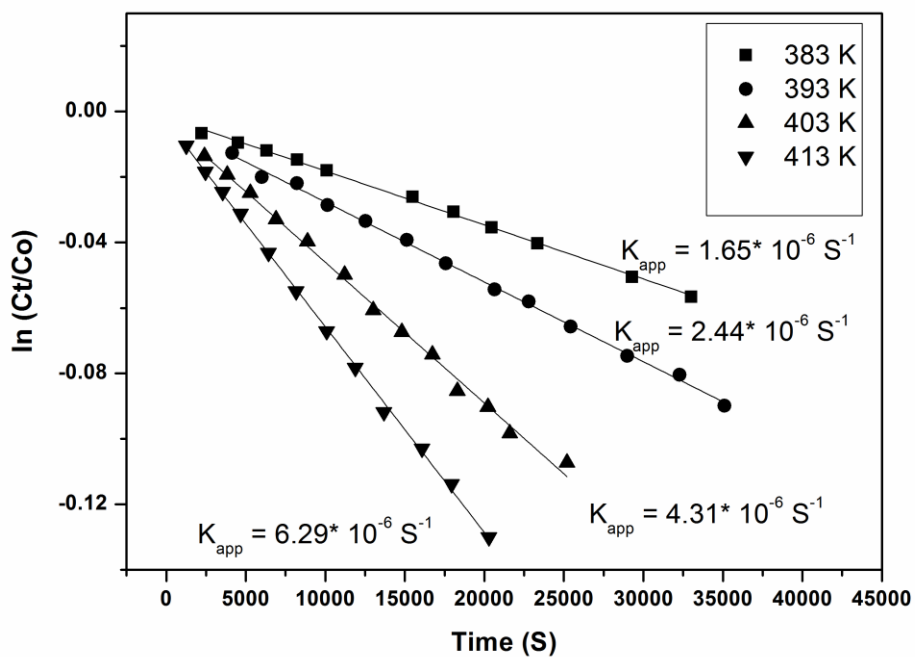


Fig S14 Reaction rates of Co-ZrSBA-15

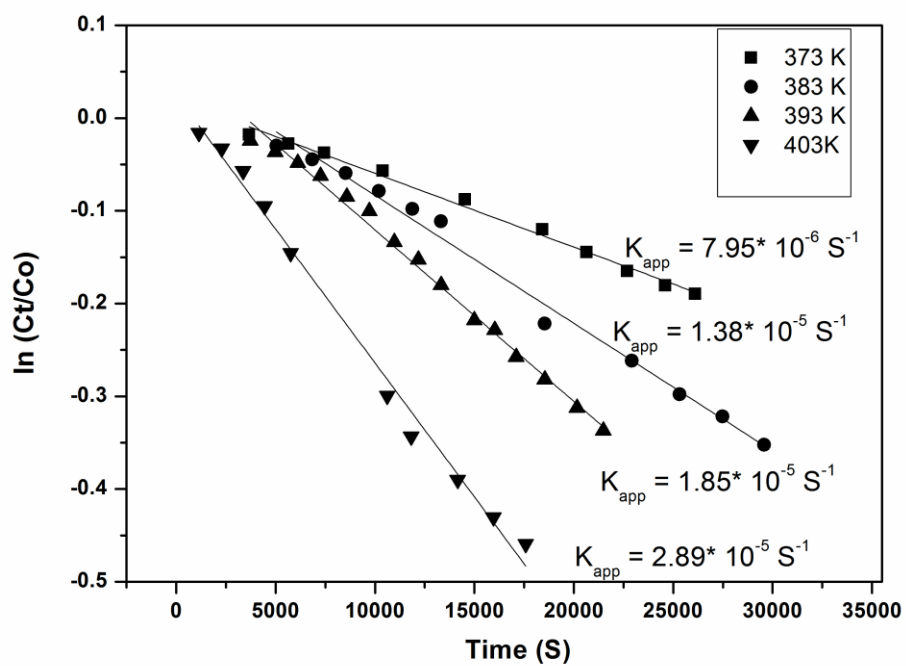


Fig S15 Reaction rates of Co-KZrSBA-15

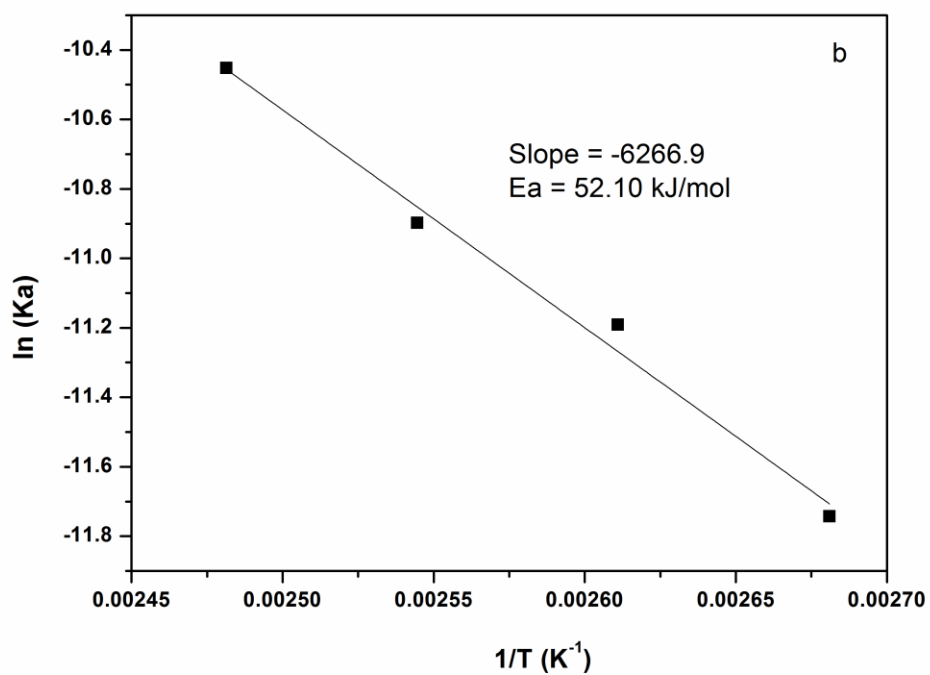
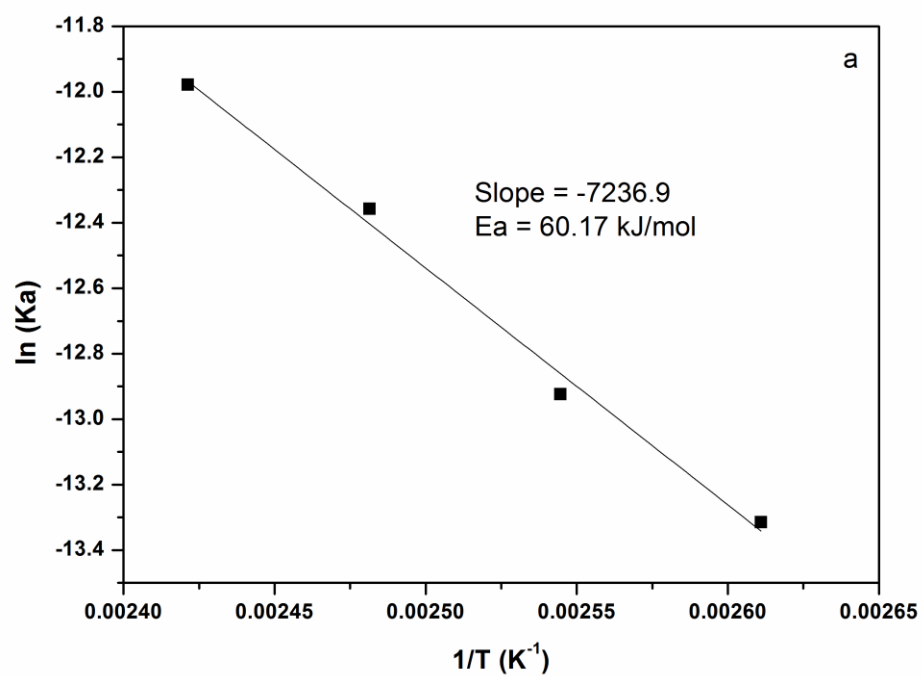
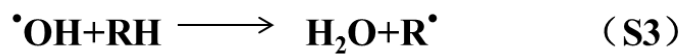


Fig. S16 Arrhenius plot of ethylbenzene oxidation catalysed by a) Co-ZrSBA-15; b) Co-KZrSBA-15

Reactions of the hydrocarbon oxidation:

**Initiation:**



**Propagation:**



**Termination:**

